

Water Vapor Permeability of Poly(lactide)s: Effects of Molecular Characteristics and Crystallinity

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ABSTRACT: Amorphous-made poly(L-lactide) [i.e., poly(L-lactic acid) (PLLA)], poly(L-lactide-co-D-lactide)-[P(LLA-DLA)](77/23), and P(LLA-DLA)(50/50) films and PLLA films with different crystallinity (X_c) values were prepared, and the effects of molecular weight, D-lactide unit content (tacticity and optical purity), and crystallinity of poly(lactide) [i.e., poly(lactic acid) (PLA)] on the water vapor permeability was investigated. The changes in number-average molecular weight (M_n) of PLLA films in the range of 9×10^4 – 5×10^5 g mol⁻¹ and D-lactide unit content of PLA films in the range of 0–50% have insignificant effects on their water vapor transmission rate (WVTR). In contrast, the WVTR of PLLA films decreased monotonically with increas-

ing X_c from 0 to 20%, while leveled off for X_c exceeding 30%. This is probably due to the higher resistance of "restricted" amorphous regions to water vapor permeation compared with that of the "free" amorphous regions. The free and restricted amorphous regions are major amorphous components of PLLA films for X_c ranges of 0–20% and exceeding 30%, respectively, resulting in the aforementioned dependence of WVTR on X_c . © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2245–2252, 2006

Key words: biodegradable polyesters; crystallization; diffusion; poly(lactide)s; water vapor permeation

INTRODUCTION

Poly(L-lactide) [i.e., poly(L-lactic acid) (PLLA)] is one of the most simplest biodegradable polyesters and has been produced from renewable resources as an alternative for traditional commercial polymers.^{1–13} It can be utilized for medical and pharmaceutical applications because of its excellent mechanical performance and very low toxicity. For commercial polymers, their physical properties, such as thermal and mechanical properties, gas permeability, etc., are crucial parameters to determine their applications. Among the gas permeability properties, water vapor permeability is an important factor, when the commercial polymers are used for food packages, containers, bottles, and so on. For poly(lactide) [i.e., poly(lactic acid) (PLA)], vast information with respect to physical properties has been accumulated. However, there have been few reports on the water vapor transmission behavior of PLA-based materials, in which the effects of molecular

characteristics and highly ordered structures were investigated.

The exceptions are the articles by Shogren,¹⁴ Siparsky et al.,¹⁵ and Auras et al.¹⁶ Shogren found that the water vapor transmission rate (WVTR) (at 25°C and 25 μ m of film thickness) of an as-cast PLLA specimen (172 g m⁻² day⁻¹) was much higher than that of a crystallized PLLA specimen (82 g m⁻² day⁻¹).¹⁴ Siparsky et al. investigated the effects of numerous parameters such as incorporated D-lactide or ϵ -caprolactone units in L-lactide polymer chains, crystallinity (X_c), and blending of PLLA on the water vapor transmission properties of the films.¹⁵ However, the X_c of PLLA specimens was in a narrow range of 8–32% (according to our method mentioned later) and the molecular weight of PLLA specimens was fixed. On the other hand, Auras et al. focused on a variety of physical properties, and therefore, measurements of water vapor transmission properties were carried out solely for typical two kinds of PLA specimens with 2% and 6% of D-lactide units.¹⁶

The purpose of this article was to investigate in detail the effects of molecular characteristics and highly ordered structures of PLA specimens on their water vapor transmission behavior. For this purpose, we have prepared PLLA having different molecular weights by polymerization of L-lactide at different conditions and by hydrolysis of relatively low molecular weight PLLA in the melt¹⁷ and synthesized or

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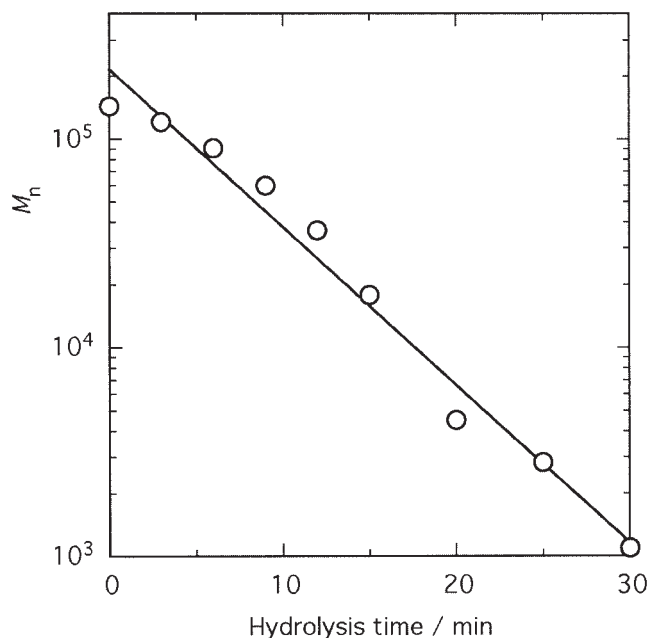


Figure 1 M_n of PLLA-L after the hydrolysis at 180°C in the melt as a function of hydrolysis time.

obtained PLA with different D-lactide contents (tacticities and optical purities). We have prepared films from these polymers by solution casting and the obtained films were made amorphous by melt-quenching or the melt-quenched films were crystallized for different times to have various X_c values.^{18–21} The WVTR values of the amorphous-made PLA films with different D-lactide unit contents (tacticities and optical purities) and PLLA films with different molecular weights and of the crystallized PLLA films with different X_c values were estimated and the effects of these structural parameters on WVTR were discussed.

EXPERIMENTAL

Materials

PLLA with the lowest molecular weight (abbreviated as PLLA-L) and P(LLA-DLA)(77/23) were kindly supplied by Unitika Co. (Kyoto, Japan). PLLA with the highest molecular weight (abbreviated as PLLA-H) and the middle molecular weight (abbreviated as PLLA-M) and P(LLA-DLA)(50/50) were synthesized by ring-opening polymerization of L-lactide and DL-lactide (equimolar mixture of L- and D-lactides), respectively, initiated with stannous octoate (0.03 wt %) and lauryl alcohol (0.3 wt %, solely for PLLA-M) for 10 h, as reported in our previous studies.^{22–24} PLLA with different molecular weights in a wide M_n range of 1.09×10^3 – 1.18×10^5 g mol⁻¹ were prepared by the hydrolysis of the purified and dried PLLA-L at 180°C in the melt for 3–30 min (Fig. 1). The PLLA-L hydrolyzed for 3 and 6 min could form films with smooth

surface and no pore after the thermal treatment mentioned later, while for the PLLA-L hydrolyzed for the periods exceeding 6 min and therefore having lower M_n values, shrinkage or pore formation took place during thermal treatment (melting process) because of the high chain mobility. These polymers were abbreviated as PLLA-L(3) and PLLA-L(6), respectively. Since PLLA-L(3) had a molecular weight similar to that of the original PLLA-L, we have used solely PLLA-L(6) among the polymers prepared by hydrolysis in the melt.

The obtained or supplied PLLA, P(LLA-DLA)(77/23), and P(LLA-DLA)(50/50) were used after purification by precipitation using dichloromethane (for PLLA) or acetone [for P(LLA-DLA)(77/23)] and P(LLA-DLA)(50/50)] and methanol as solvent and nonsolvent, respectively, followed by drying in vacuo for 1 week. The films (thickness of ~ 50 μ m) obtained by a solution-casting method using methylene chloride as a solvent were made amorphous or crystallized by the following procedures. The films in Teflon petri dishes were melted at 250°C for 5 min and then quenched at 0°C or the melt-quenched films were crystallized at 140°C for 2.5–12.5 min, followed by quenching at 0°C to stop further crystallization.^{18–21}

Measurements

The weight- and number-average molecular weights (M_w and M_n , respectively) and the molecular weight distribution of the polymers were evaluated in chloroform at 40°C by a Tosoh GPC system (Tokyo, Japan; refractive index monitor: RI-8020) with two TSK Gel columns (GMH_{XL}) using polystyrene standards. The specific optical rotation of the polymers was measured in chloroform at 25°C and a wave length of 589 nm ($[\alpha]_{589}^{25}$) using a JASCO (Tokyo, Japan) DIP-140 polarimeter. The L-lactyl unit (a half L-lactide unit) fraction X_L (mol %) of the polymers was evaluated using the following equations:^{22–24}

$$X_L(\text{mol } \%) = 100([\alpha]_{589}^{25} - 156)/(-156 - 156) \quad (1)$$

where -156 deg dm⁻¹ g⁻¹ cm³ is a $[\alpha]_{589}^{25}$ value reported for PLLA.^{22,24} Averaged L- and D-lactyl unit sequence lengths (l_L and l_D , respectively) were estimated by the use of following equations, assuming that LLA and DLA units were polymerized by their random addition and no ester exchange reaction occurred during polymerization:^{24,25}

$$l_L = 2/(1 - X_L/100) \quad (2)$$

$$l_D = 2/(X_L/100) \quad (3)$$

TABLE I
Molecular Characteristics and Thermal Properties of PLLA and PLA Films after Thermal Treatment

Code	Crystallization time ^a (min)	X_L^b (%)	$[\alpha]_{589}^{25}$ (deg dm ⁻¹ g ⁻¹ cm ³)	l_L^c (lactyl unit)	M_n (g mol ⁻¹)	M_w/M_n	X_c^d (%)	T_g^d (°C)	T_{cc}^d (°C)	T_m^d (°C)
PLLA-H ^e	0	99.7 ^f	-155 ^f	667 ^f	4.78×10^5	1.88	0.6	56.3	110.9	177.3
PLLA-M ^e	0	99.7 ^f	-155 ^f	667 ^f	1.54×10^5	1.58	1.7	58.8	109.3	177.2
PLLA-L ^e	0	99.4 ^f	-154 ^f	333 ^f	1.25×10^5	1.62	0.7	59.5	129.3	167.7
	2.5				1.21×10^5	1.69	0.7	58.6	124.0	167.2
	5.0				1.30×10^5	1.61	5.7	58.6	120.1	166.8
	7.5				1.11×10^5	1.81	19.1	58.2	117.3	167.6
	10				1.24×10^5	1.66	32.0	59.1		167.4
	12.5				1.25×10^5	1.65	34.9	57.1		167.2
PLLA-L(6) ^e	0				9.23×10^4	1.70	1.0	57.4	129.7	167.8
P(LLA-DLA) (77/23) ^g	0	77.2 ^f	-85 ^f	8.8 ^f	1.17×10^5	1.62	0.0	52.5		
P(LLA-DLA) (50/50) ^g	0	50.0 ^f	0 ^f	4.0 ^f	1.66×10^5	1.76	0.0	53.3		

^a Crystallization time = 0 means that the specimens were melt-quenched.

^b L-lactyl unit content X_L of P(LLA-DLA) was obtained using the following equation: $X_L = 100 ([\alpha]_{589}^{25} - 156) / -156 - 156$.

^c Average L-lactyl unit sequence length (l_L) of P(LLA-DLA) was obtained using the following equation: $l_L = 2 / (1 - X_L/100)$.

^d The crystallinity, glass transition, cold crystallization, and melting temperatures (X_c , T_g , T_{cc} , and T_m , respectively) were obtained from the DSC first run.

^e Poly(L-lactide) (PLLA).

^f These values are for the specimens before thermal treatment.

^g Poly(L-lactide-co-D-lactide) [P(LLA-DLA)].

The glass transition, cold crystallization, and melting temperatures (T_g , T_{cc} , and T_m , respectively) and enthalpies of cold crystallization and melting (ΔH_{cc} and ΔH_m) of the films were determined by a Shimadzu (Kyoto, Japan) DSC-50 differential scanning calorimeter. The films (sample weight of ~3 mg) were heated at a rate of 10°C min⁻¹ under a nitrogen gas flow at a rate of 50 mL min⁻¹. T_g , T_{cc} , T_m , ΔH_{cc} , and ΔH_m values were calibrated using benzophenone, indium, and tin as standards. The X_c of the films was evaluated according to the following equation, assuming that D-lactyl units as well as L-lactyl units can crystallize:^{26,27}

$$X_c(\%) = 100(\Delta H_{cc} + \Delta H_m) / 135 \quad (4)$$

where 135 J g⁻¹ is ΔH_m of PLLA crystal having infinite size reported by Miyata and Masuko.²⁸ By definition, ΔH_{cc} and ΔH_m are negative and positive, respectively. The characteristics and properties of the films after the thermal treatment are summarized in Table I. To obtain information for the changes in T_g of the films through water absorption during WVTR measurements, we estimated T_g of the films after immersion in distilled water for 24 h at 25°C. The immersion time of 24 h was selected because the water absorption of PLLA films is reported to saturate in 24 h.²⁹ Although the decreases in T_g by 2–10°C were observed for water-absorbed PLLA films after immersion in distilled

water for 24 h, the T_g values in the water-absorbed state were far apart from the temperature for WVTR measurements (25°C). Therefore, it seems that such small decreases in T_g during the WVTR measurements did not largely alter the WVTR values of the films.

The WVTR values of the films were measured as described in JIS (Japanese Industrial Standard) Z 0208 (Dish Method: Testing Methods for Determination of the Water Vapor Transmission Rate of Moisture-Proof Packaging Materials) with the cups purchased from Imoto Machinery Co. Ltd. (Kyoto, Japan) using a constant temperature and humidity chamber IG400 (Yamato Scientific Co. Ltd., Tokyo, Japan). Here, we selected Condition A of Z 0208. Namely, the WVTR measurements were carried out at 25°C under a gradient of 90% of relative humidity (r.h.) outside the cup (inside the constant temperature and humidity chamber) and 0% r.h. inside the cup (calcium chloride, anhydrous; Kishida Chemical Co. Ltd., Tokyo, Japan) across the film. The calcium chloride used here came up to the standard of JIS K 8123 and were sieved to have the particle size of 590–2380 μm (JIS Z 8801) before the WVTR measurements. The procedure for the measurements is briefly mentioned here. The calcium chloride was put into the cup (60 mm in inside diameter, 15 mm in depth) which was completely dried and heated to 30–40°C. The amount of the cal-

TABLE II
Normalized Water Vapor Transmission Rate (WVTR) and Water Vapor Permeation Coefficient (P) of PLLA and PLA films at 25°C

Code	Crystallization time ^a (min)	Normalized WVTR ^b (g/m ² /day)	$P \times 10^{14}$ (kg m/m ² /s/Pa)
PLLA-H ^c	0	228	2.08
PLLA-M ^c	0	210	1.92
PLLA-L ^c	0	239	2.18
	2.5	220	2.01
	5.0	208	1.90
	7.5	125	1.14
	10	108	0.99
	12.5	114	1.04
PLLA-L(6) ^c	0	209	1.91
P(LLA-DLA)(77/23) ^d	0	208	1.90
P(LLA-DLA)(50/50) ^d	0	214	1.95

^a Crystallization time = 0 means that the specimens were melt-quenched.

^b Water vapor transmission rate normalized at thickness of 25 μm .

^c Poly(L-lactide) (PLLA).

^d Poly(L-lactide-co-D-lactide) [P(LLA-DLA)].

cium chloride inside the cup was controlled to have a final gap ~ 3 mm between the calcium chloride particles and the film. The film was placed on the cup and sealed with molten paraffin ($T_m = 52$ – 56°C ; Nacalai Tesque Inc., Kyoto, Japan) and then the cup with the film and calcium chloride was kept in the constant temperature and humidity chamber (25°C and 90% of r.h.). The weight of the cup with the film and calcium chloride was measured every 24 h for the periods up to 96 h. Thus obtained WVTR ($\text{g m}^{-2} \text{day}^{-1}$) values were normalized to a film thickness of 25 μm , using the following equation for comparison with the reported values.¹⁴

$$\text{Normalized WVTR} = \text{Non-normalized WVTR} \times l/25 \quad (5)$$

where l (μm) is the actual film thickness. All the WVTR values shown here are normalized. On the other hand, water vapor permeability coefficient (P) was calculated using the following equation:¹⁶

$$P = \text{Non-normalized WVTR} \times l/\Delta P \quad (6)$$

where WVTR and l are expressed by units of $\text{kg m}^{-2} \text{s}^{-1}$ and m, respectively, ΔP is the difference between the water vapor partial pressure across the film (Pa).¹⁶ The experimental values of WVTR and P values represent averages of measurements from the three replicate samples. The normalized WVTR and P values are tabulated in Table II.

RESULTS AND DISCUSSION

Effects of molecular weights

Figure 2 shows DSC thermograms of amorphous-made PLLA with different molecular weights. All the

DSC thermograms of amorphous-made PLLA films have glass transition, cold crystallization, and melting peaks in the temperature ranges of 50 – 60°C , 100 – 130°C , and 160 – 180°C , respectively. The peak areas of cold crystallization and melting were very similar for all the films, reflecting that these films were amorphous after thermal treatment. Actually, the estimated X_c values were $\sim 0\%$ for all PLLA films having different molecular weights, as summarized in Table I. The typical time changes of the water vapor transmitted through an amorphous-made PLLA films with different M_n values are shown in Figure 3. It is seen that the amount of transmitted water increased linearly with time. This means that the amount of water absorbed to calcium chloride had no significant effect on water vapor transmission. The difference in slope between the two films is due to the thickness difference between them. We have estimated normalized WVTR from the slopes of the experimental data.

The normalized WVTR of the amorphous-made PLLA films are plotted in Figure 4 as a function of M_n . It is seen that in the M_n range studied here ($M_n = 9.2 \times 10^4$ – $4.8 \times 10^5 \text{ g mol}^{-1}$) M_n had insignificant effects on the normalized WVTR of PLLA films. In other words, an increase in the number of hydrophilic terminal groups (carboxyl and hydroxyl groups) per unit weight from 4.2×10^{-6} [$2/(4.8 \times 10^5)$] to 2.2×10^{-5} [$2/(9.2 \times 10^4)$] mol g^{-1} will not alter the normalized WVTR of PLLA films. Such insignificant effects are very similar to the effects of M_n on surface hydrophilicity of amorphous-made PLLA films.³⁰ Furthermore, considering this result, as far as the M_n or the density of the hydrophilic terminal groups of amorphous-made PLLA films is in this range, WVTR of amorphous-made PLLA films remains constant even if their hydrolysis takes place during their use. The obtained

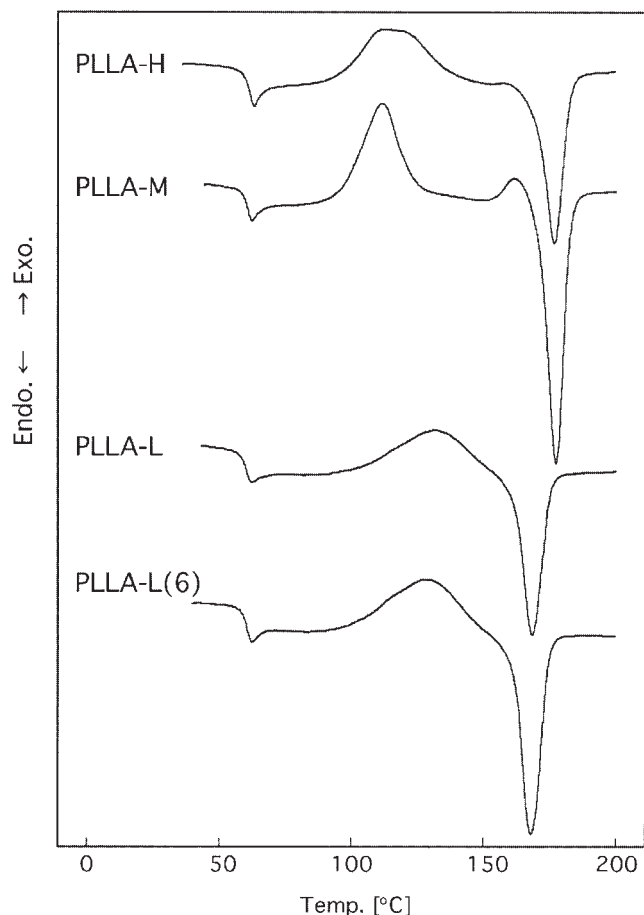


Figure 2 DSC thermograms of amorphous-made PLLA films with different molecular weights [PLLA-H, PLLA-M, PLLA-L, and PLLA(6) films].

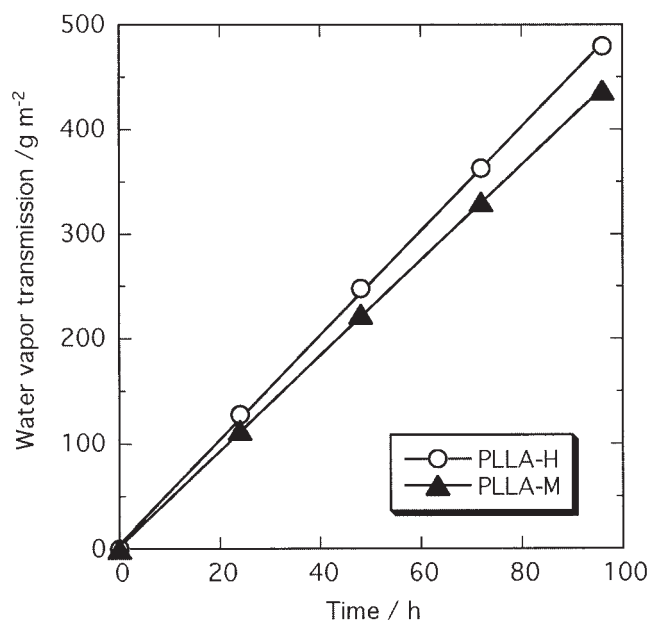


Figure 3 Water vapor transmission through amorphous-made PLLA films [PLLA-H film ($M_n = 4.54 \times 10^5 \text{ g mol}^{-1}$ and film thickness = $53 \mu\text{m}$) and PLLA-M film ($M_n = 1.42 \times 10^5 \text{ g mol}^{-1}$ and film thickness = $61 \mu\text{m}$)] as a function of time.

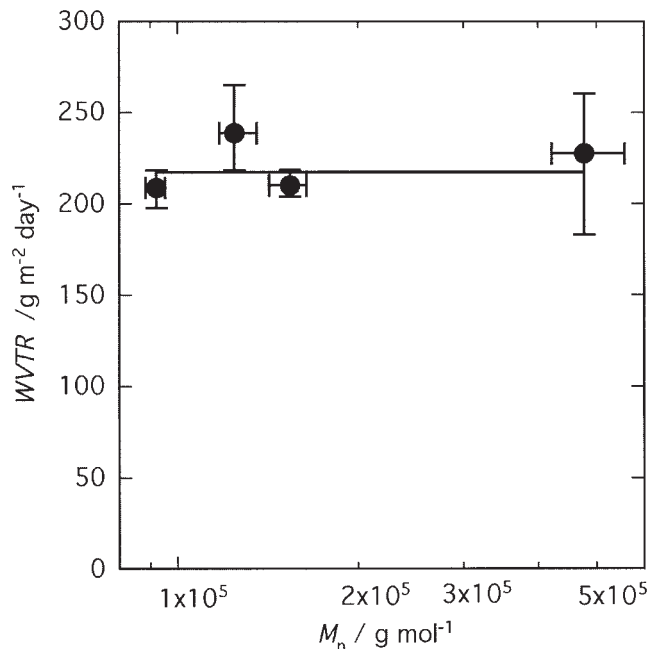


Figure 4 Effects of number-average molecular weight (M_n) on normalized water vapor transmission rate (WVTR) of amorphous-made PLLA films.

normalized WVTR values for the amorphous-made PLLA films $209\text{--}239 \text{ g m}^{-2} \text{ day}^{-1}$ for a gradient from 90% to 0% r.h. are slightly higher than the reported value $172 \text{ g m}^{-2} \text{ day}^{-1}$ for an as-cast PLLA film at the same temperature for a gradient from 100% to 0% r.h.¹⁴ Our higher normalized WVTR values may be due to the low X_c values of our specimens compared with that prepared in the article or the method difference in WVTR measurements. We could not measure the WVTR values of films prepared by hydrolysis of PLLA-L at 180°C in the melt for the periods exceeding 6 min and having M_n lower than $\sim 9 \times 10^4 \text{ g mol}^{-1}$ because of the brittleness of the films in addition to the reasons mentioned earlier. This can be expected from a reported result for the effects of M_w or M_n on tensile strength of PLLA or poly(D-lactide),³¹ in which the tensile strength became practically nil when the M_w and M_n of PLLA or poly(D-lactide) were lowered to $\sim 5 \times 10^4$ and $3 \times 10^4 \text{ g mol}^{-1}$, respectively.

Effects of D-lactide unit content

Figure 5 illustrates the DSC thermograms of amorphous-made PLA films with different D-lactide unit contents. PLLA-L film had glass transition, cold crystallization, and melting peaks, while P(LLA-DLA)(77/23) and P(LLA-DLA)(50/50) films yield solely a glass transition peak, reflecting that P(LLA-DLA)(77/23) and P(LLA-DLA)(50/50) films were amorphous and had no or very low crystallizability. The normalized WVTR of the PLA films are plotted in Figure 6 as a

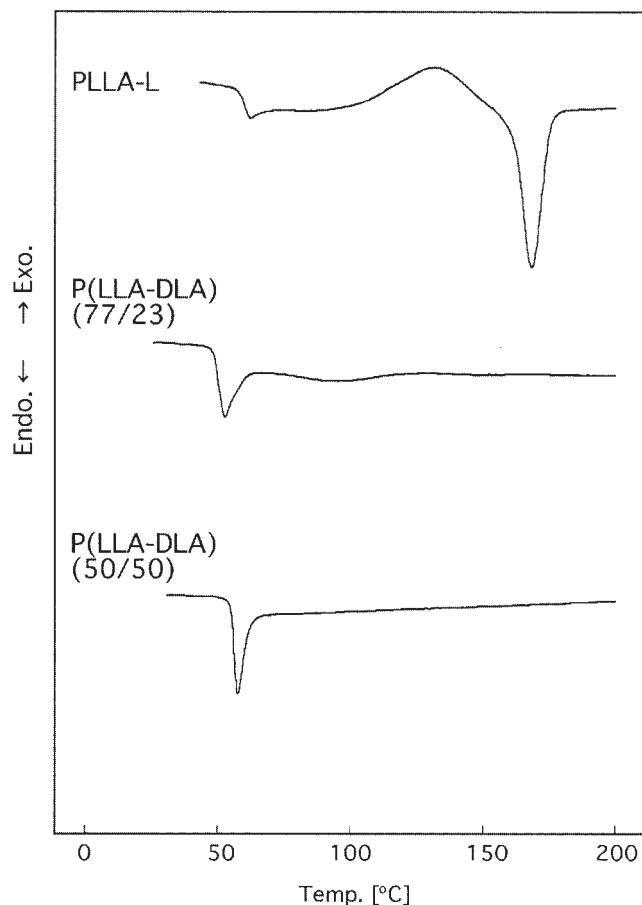


Figure 5 DSC thermograms of amorphous-made PLA films with different D-lactide unit contents (tacticity or optical purity) [PLLA-L, P(LLA-DLA)(77/23), and P(LLA-DLA)(50/50) films].

function of D-lactide unit content. Analogous with the M_n effects, D-lactide unit content (tacticity and optical purity) had practically insignificant effects on normalized WVTR of PLA films. The P values for P(LLA-DLA)(98/2) and P(LLA-DLA)(94/6) estimated by Auras *et al.* were very similar with each other at two different temperatures [1.89×10^{-14} and 1.89×10^{-14} kg m/m² s Pa at 20°C and 1.65×10^{-14} and 1.61×10^{-14} kg m/m² s Pa at 30°C]. Such negligibly small effects of incorporated D-lactide unit content (tacticity and optical purity) on P are comparable with our result for PLLA-L, P(LLA-DLA)(77/23), and P(LLA-DLA)(50/50) films [2.18×10^{-14} , 1.90×10^{-14} , and 1.95×10^{-14} kg m/m² s Pa, respectively, (Table II)]. On the other hand, Shogren reported that the normalized WVTR values of the as-cast and annealed PLLA films (82 and 172 g m⁻² day⁻¹, respectively) are higher than that of poly(3-hydroxybutyrate-co-3-valerate) (PHBV) having 6%, 12%, and 18% valerate units (13–26 g m⁻² day⁻¹), comparable with that of poly(ϵ -caprolactone) (PCL) (177 g m⁻² day⁻¹), and lower than that of Bionolle (330 g m⁻² day⁻¹).¹⁴ Therefore,

the reported result and the results obtained in Figures 4 and 6 indicate that the kind of monomer units is a crucial parameter to determine the WVTR of the biodegradable polyester films rather than their molecular weight or tacticity.

Effects of crystallinity

Figure 7 shows the DSC thermograms of melt-quenched PLLA-L films crystallized for different times at 140°C. As mentioned earlier, for noncrystallized or melt-quenched PLLA-L film (crystallization time = 0 min) three peaks (glass transition, cold crystallization, and melting peaks) were observed, while for the crystallized PLLA-L films, cold crystallization peak became smaller with crystallization time and finally disappeared at crystallization times exceeding 7.5 min. The disappearance of cold crystallization peak means the complete consumption of crystallizable “free” amorphous regions outside the spherulites in the films. The estimated X_c of PLLA films increased monotonically with crystallization time, as listed in Table I. The normalized WVTR of the PLLA-L films are plotted in Figure 8 as a function of X_c . In our previous article, the crystallinity increases of PLLA specimens were in the range of 4–9% in 12 months when they were hydrolytically degraded in phosphate buffered solution at 37°C.²⁰ Assuming linear increases of X_c in 12 months, X_c increases are calculated to be 0.01–0.02% in 24 h. Therefore, it seems that such insignificant increases in X_c of PLLA specimens during

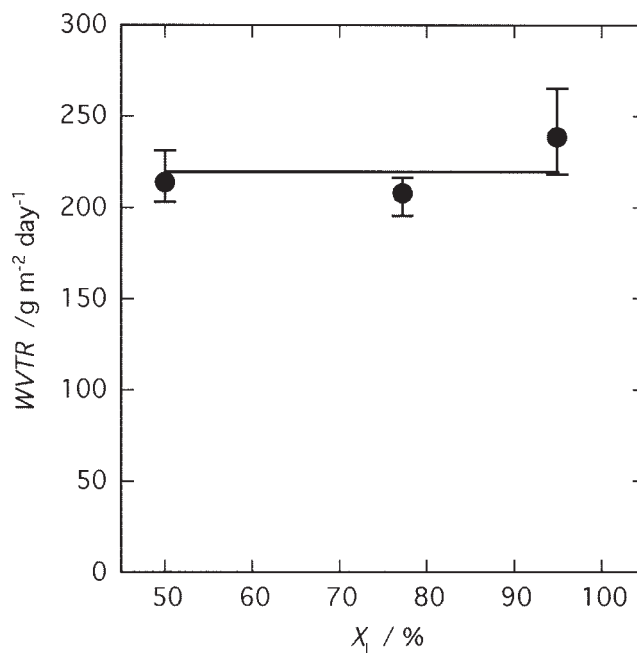


Figure 6 Effects of D-lactide unit content (tacticity or optical purity) on normalized water vapor transmission rate (WVTR) of amorphous-made PLA films.

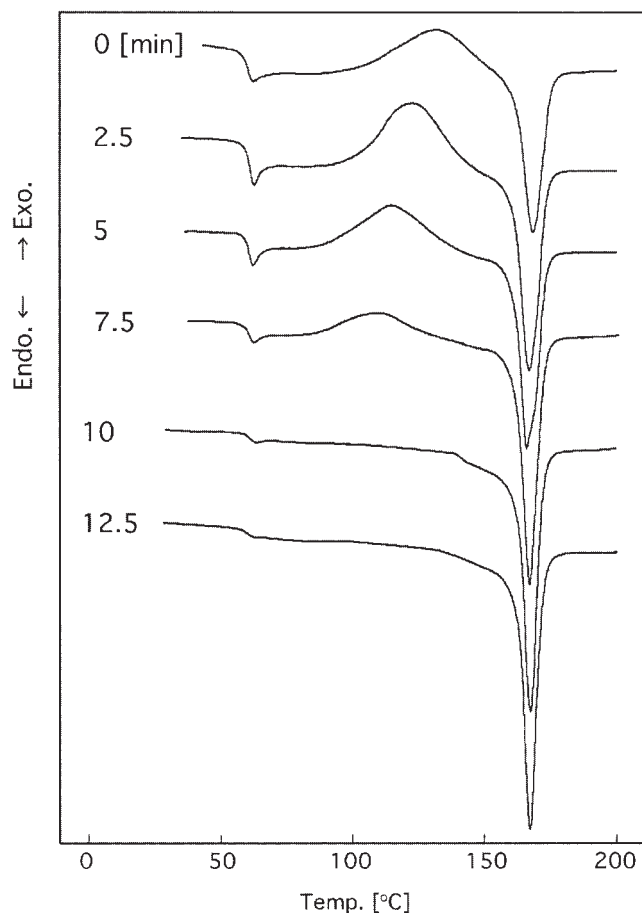


Figure 7 DSC thermograms of melt-quenched PLLA-L films crystallized at 140°C for different times.

the measurements did not affect the estimation of WVTR values.

As seen in Figure 8, the WVTR of PLLA films decreased rapidly and monotonically from 230 to 130 $\text{g m}^{-2} \text{day}^{-1}$, with increasing X_c from 0 to 20%, while the WVTR of PLLA films leveled off at around 110 $\text{g m}^{-2} \text{day}^{-1}$ for X_c exceeding 30%. The decrease in normalized WVTR of PLLA film by annealing has been reported by Shogren; in the article, the normalized WVTR value for the as-cast PLLA film (172 $\text{g m}^{-2} \text{day}^{-1}$) decreased to 82 $\text{g m}^{-2} \text{day}^{-1}$ by annealing at 130°C for 10 min.¹⁴ However, he did not evaluate the X_c values of the specimens. Our lowest normalized WVTR value ($\sim 110 \text{ g m}^{-2} \text{day}^{-1}$) is significantly higher than that (82 $\text{g m}^{-2} \text{day}^{-1}$) reported by Shogren for the annealed PLLA film. As mentioned earlier, the reason for our higher WVTR values even for the highest X_c value may be the lower X_c of our specimens or the difference in WVTR measurement method. Such dependence of X_c on WVTR of PLLA films in Figure 8 is very similar to that on enzymatic hydrolysis rate of PLLA films in the presence of proteinase K (R_{EH}) as shown in Figure 9.²¹ Here, for uniformity of the X_c values in the present study and the previous article,

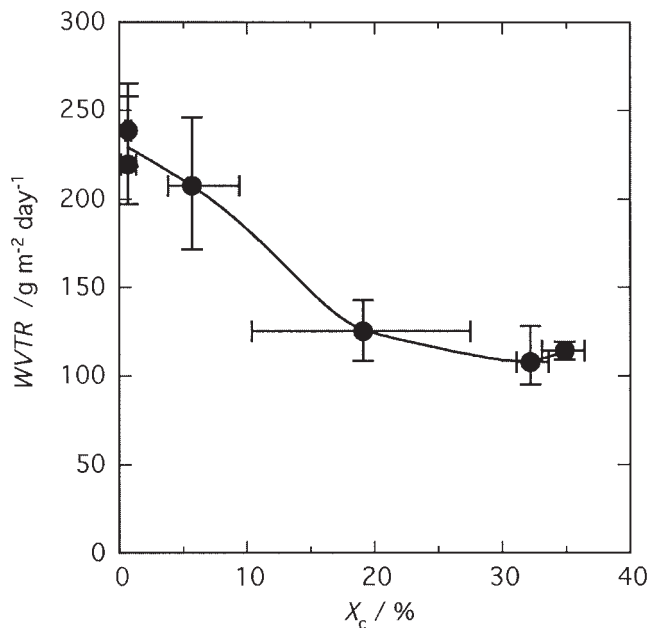


Figure 8 Effects of crystallinity (X_c) on normalized water vapor transmission rate (WVTR) of PLLA-L films.

the X_c values estimated in the previous article with 93 J g^{-1} reported by Fischer *et al.* for ΔH_m value of PLLA crystal having an infinite size³² were recalculated with

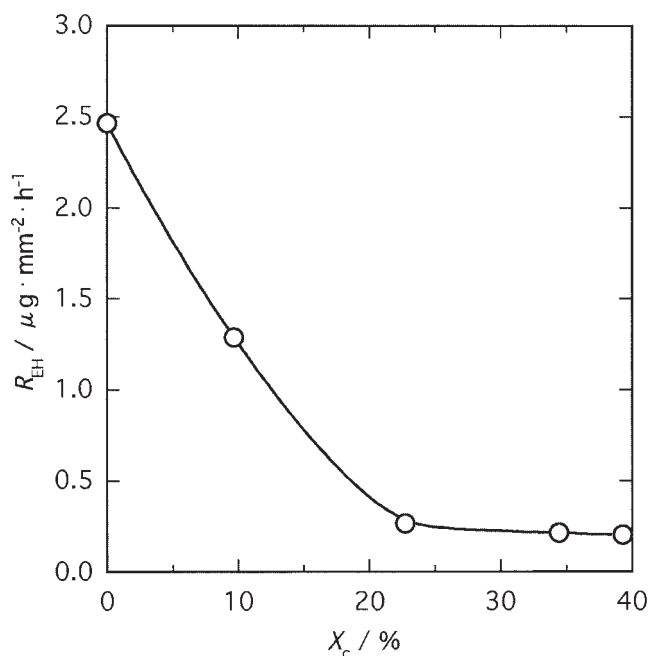


Figure 9 Effects of crystallinity (X_c) on enzymatic hydrolysis rate (R_{EH}) of PLLA films.²¹ Here, for uniformity of the X_c values in the present study and the previous article,²¹ the X_c values estimated in the previous article with 93 J g^{-1} reported by Fischer *et al.* for ΔH_m value of PLLA crystal having infinite size³² were recalculated with 135 J g^{-1} reported by Miyata and Masuko.²⁸

135 J g⁻¹ reported by Miyata and Masuko.²⁸ The R_{EH} of PLLA films decreased rapidly and monotonically from 2.5 to 0.27 $\mu\text{g mm}^{-2} \text{h}^{-1}$, with increasing X_c from 0 to 20%, while leveled off at around 0.20 $\mu\text{g mm}^{-2} \text{h}^{-1}$ for X_c exceeding 30%.

This nonlinear dependence of R_{EH} on X_c was ascribed to the large difference in enzymatic hydrolyzability between the free amorphous regions as in a completely amorphous specimen and the "restricted" amorphous regions between the crystalline regions in the spherulites.²¹ Namely, for X_c below 20%, the amorphous regions are composed mainly of free amorphous regions whose enzymatic hydrolyzability is high, while X_c exceeding 30%, the amorphous regions consist solely of restricted amorphous regions whose enzymatic hydrolyzability is very low. This can explain the nonlinear dependence of R_{EH} on X_c . Such low enzymatic hydrolyzability of the restricted amorphous regions has been attributed to the high hydrolysis-resistance of folding chains contained in the restricted amorphous regions. Similar dependence of normalized WVTR on X_c strongly suggests that the restricted amorphous regions have a higher resistance to water vapor permeation compared with that of the free amorphous regions. Such higher resistance of restricted amorphous regions to water vapor permeation may be due to the fact that they contain specific amorphous regions called "crystalline-amorphous interfacial regions" or "transition regions between crystalline and amorphous regions," whose mobility is highly restricted by adjacent crystalline regions.^{33,34}

CONCLUSIONS

From the experimental results mentioned earlier, the following conclusions can be derived for WVTR of PLA films:

1. The changes in M_n of PLLA films in the range of 9×10^4 – 5×10^5 g mol⁻¹ and D-lactide unit content of PLA films in the range of 0–50% have insignificant effects on their WVTR values.
2. The WVTR of PLLA films decreased monotonically with increasing X_c from 0 to 20%, while leveled off for X_c exceeding 30%. This is probably due to the higher resistance of restricted amorphous regions to water vapor permeation compared with that of the free amorphous regions. The free and restricted amorphous regions are major amorphous components in PLLA films for X_c ranges of 0–20% and exceeding 30%, respectively, resulting in the aforementioned dependence of WVTR on X_c .

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