Physical Properties and Enzymatic Hydrolysis of Poly(L-lactide)–TiO2 Composites

Norio Fukuda,[1] Hideto Tsuji[2]

[1]*Aichi Industrial Technology Institute, Nishishinwari, Hitotsugi-cho, Kariya, Aichi 448-0003, Japan*
[2]*Department of Ecological Engineering, Faculty of Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan*

ABSTRACT: Amorphous poly(L-lactide) (PLLA) composite films with titanium dioxide (TiO_2) particles were prepared by solution-casting using methylene chloride as a solvent, followed by quenching from the melt. The effects of surface treatment, volume fraction, size, and crystalline type of the TiO_2 particles on the mechanical properties and enzymatic hydrolysis of the composite films were investigated. The tensile strength of the PLLA composite films containing TiO_2 particles except for anatase-type ones with a mean particle size of 0.3–0.5 μm was lowered and the Young's modulus became higher with increasing the content of TiO_2 particles. The tensile strength of the composite films containing anatase-type TiO_2 with a mean particle size of 0.3–0.5 μm at contents of 20 wt % or less was almost the same as that of the pure PLLA film. The enzymatic hydrolysis of PLLA matrix was accelerated by the addition of the hydrophilic anatase-type TiO_2 particles (nontreated or Al_2O_3 treated) with a mean particle size of 0.3–0.5 μm at relatively high contents such as 20 wt %. On the other hand, the enzymatic hydrolysis of PLLA matrix was inhibited by composite formation with the hydrophobic rutile-type TiO_2 particles (Al_2O_3-stearic acid treated, or ZrO_2-Al_2O_3-stearic acid treated). These results suggest that the mechanical properties and enzymatic hydrolyzability of the PLLA can be controlled by the kind and amount of the added TiO_2 particles. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 190–199, 2005

Key words: poly(L-lactide); titanium dioxide; composites; biodegradable; mechanical properties

INTRODUCTION

The field of biodegradable polymers has attracted a good deal of attention from the viewpoint of the solution for the environmental issues on nondegradable plastics waste. Poly(L-lactide) (PLLA) has been one of the most promising biodegradable and biocompatible polymers because of the excellent processability and high mechanical properties comparable with those of polyethylene and polystyrene.[1–6] For last several years, applications of PLLA have spread in commodity areas, such as packaging films and bottles, as well as in the biomedical field, such as drug delivery systems and scaffolds for tissue regeneration.[7–10]

Most of the enzymatic hydrolysis studies of PLLA have been conducted using proteinase K, which is a fungal protease from the mold *Tritirachium album*.[11] The enzymatic hydrolysis of PLLA is affected by a variety of factors, including highly ordered structures, molecular characteristics, and polymer blending.[6,12] The enzymatic hydrolysis rate of PLLA is faster in the amorphous region than in the crystalline region.[12–16]

Iwata and Doi[17] studied the enzymatic hydrolysis of PLLA single crystals using proteinase K and concluded that their enzymatic hydrolysis proceeds at the disordered chain packing region of the crystal edges rather than at their chain folding surfaces.

Recently, we have prepared the PLLA–$CaCO_3$ composite films and investigated the enzymatic hydrolysis and mechanical properties.[18] It was revealed that the addition of $CaCO_3$ particles at concentrations below 10 wt % led to the acceleration of the enzymatic hydrolysis of PLLA with a maintenance of the mechanical properties.

TiO_2 can be used as the additive for polymers, similarly to $CaCO_3$. TiO_2 is a characteristic filler with three crystalline phases, anatase, rutile and brookite, and is obtained in different sizes, shapes, and surface treatments. It is generally accepted that ultrafine anatase-type TiO_2 with a mean particle size less than 0.1 μm exhibits a higher photocatalytic activity than rutile-type TiO_2,[19] whereas rutile-type TiO_2 is a more suitable material for white pigments and coatings because of its great refractivity and notable chemical inertia.[20] The diverse characteristics are anticipated to provide the different properties for the polymer–TiO_2 composites. In this paper, the PLLA composite films containing different TiO_2 particles were prepared, and their physical properties and biodegradability were com-

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Correspondence to: H. Tsuji (tsuji@eco.tut.ac.jp).

TABLE I
Characteristics of TiO$_2$ Particles Used in This Study

Abbreviation	Commercial grade	Crystalline phase	Surface treatment	Mean particle size (μm)
55N	TTO-55(N)		No	0.03–0.05
55A	TTO-55(A)		Al$_2$O$_3$	0.03–0.05
55C	TTO-55(C)	Rutile	Al$_2$O$_3$ and stearic acid	0.03–0.05
S-2	TTO-S-2		ZrO$_2$, Al$_2$O$_3$ and stearic acid	0.01–0.02, 0.05–0.1[a]
M-2	TTO-M-2		ZrO$_2$, Al$_2$O$_3$ and stearic acid	0.03–0.05, 0.1–0.25[a]
D-2	TTO-D-2		ZrO$_2$, Al$_2$O$_3$ and stearic acid	0.04–0.07, 0.2–0.3[a]
KA10C	KA-10C	Anatase	No	0.3–0.5
KA20	KA-20		Al$_2$O$_3$	0.3–0.5

[a] S-2, M-2, and D-2 are spindle-shaped particles, and therefore these mean particle sizes are those along the minor and the major axes, respectively.

pared with those of the pure PLLA film. All the films used in this study were made amorphous, since their mechanical properties and biodegradability are influenced by the highly ordered structures, especially by the crystallinity (χ_c).[6,12–16,21,22] To our knowledge, this is the first paper to address the enzymatic hydrolysis of PLLA composites containing TiO$_2$ particles.

EXPERIMENTAL PROCEDURES

Materials

PLLA pellets with weight-average molecular weight (M_w) = 2.6 × 10^5 g mol^{-1} (LACTY ^{TM}5000) were kindly supplied by Shimadzu Co. Ltd. (Kyoto, Japan) and used after purification by precipitation using chloroform and methanol as solvent and nonsolvent, respectively. TiO$_2$ particles used in this study are listed in Table I. KA10C and KA20 were supplied by Titan Kogyo Corp., LTD (Yamaguchi, Japan), and the other TiO$_2$ particles were gifts from Ishihara Sangyo Corp., LTD. (Osaka, Japan). 55N, 55A, 55C, S-2, M-2, and D-2 are in the rutile crystalline phase, while KA10C and KA20 are in the anatase crystalline phase. The mean particle size of the anatase-type TiO$_2$ particles is 0.3–0.5 μm (Table I), and therefore they have no significant photocatalytic activity. Some TiO$_2$ particles are surface treated with stearic acid to improve the compatibility of the particles with the polymer matrix to some extent, with Al$_2$O$_3$ and stearic acid to inhibit the photocatalytic activity of TiO$_2$ particles and with ZrO$_2$ to enhance the refractivity.

Preparation of PLLA composites with TiO$_2$

The TiO$_2$ particles dispersed into methylene chloride by ultrasonication at a concentration of 0.05 g/mL were mixed with methylene chloride solution of PLLA having the same concentration at specific ratios. The solution was sonicated and was cast on a petri dish, followed by solvent evaporation at room temperature within 1 day. The solvent trapped in the resulting films was extracted with methanol and dried *in vacuo* for a few days. The as-cast films were compression molded at 200°C using a press equipped with heating plates, according to the method previously reported.[18] The films with ~ 300 μm thickness were exclusively used except for the evaluation of the effects of the film thickness on the enzymatic hydrolysis in which the films with 150 μm thickness were used (see Table III). As it has been reported that the mechanical properties and hydrolysis behavior of PLLA are affected by its χ_c,[6,12–16,21,22] all the films used in this study were made amorphous by quenching in cold water from the melt to exclude the influence of the χ_c on the properties and enzymatic hydrolysis of pure PLLA and its composite films.

Enzymatic hydrolysis of PLLA composite films

Enzymatic hydrolysis test was conducted according to the procedure described previously.[18,23] Each of films (10 × 10 mm^2) was placed in a vial filled with 5 mL of 50 mM Tris–HCl buffer (pH8.6) containing 1 mg of proteinase K (Sigma, lyophilized powder) from the mold *T. album* and 1 mg of sodium azide. The films were incubated at 37°C with shaking for up to 24 h. The hydrolyzed films were carefully rinsed with distilled water and dried under reduced pressure to a constant weight.

The enzymatic hydrolysis rates of the films were investigated by determining the nonnormalized and normalized weight losses by the following expressions:

Nonnormalized weight loss (μg/mm^2)

$$= (W_b - W_a)/S_b \quad (1)$$

where W_b, W_a, and S_b represent the weights of the films before and after hydrolysis and the initial surface area of the films, respectively.

Normalized weight loss (μg/mm^2)

$$= \text{(nonnormalized weight loss)}$$
$$\times X_{PLLA}/(V_{PLLA})^{2/3} \quad (2)$$

$$X_{PLLA} = W_{PLLA}/(W_{TiO_2} + W_{PLLA}) \quad (3)$$

$$V_{PLLA} = (W_{PLLA}/\rho_{PLLA})/(W_{TiO_2}/\rho_{TiO_2} + W_{PLLA}/\rho_{PLLA}) \quad (4)$$

where W_{PLLA}, W_{TiO_2}, ρ_{TiO_2}, and ρ_{PLLA} represent the weights of PLLA and TiO$_2$ in the films before hydrolysis and the specific gravities of TiO$_2$ and PLLA, respectively. The ρ_{TiO_2} values of anatase and rutile type TiO$_2$ are 4.2 and 3.9 g/cm^3, respectively, while ρ_{PLLA} is 1.2 g/cm^3. The normalized weight losses were calculated on the assumption that the ratio of PLLA/TiO$_2$ removed from the films was the same as that before hydrolysis.

Measurements and observation

The M_w and number-average molecular weight (M_n) of the films were evaluated in chloroform at 40°C with a Tosoh GPC system (refractive index monitor: RI-8020) with TSK Gel columns (GMH$_{XL}$×2) using polystyrene as a standard. After melt-quenching, the molecular weights and distribution of the PLLA matrix for the composite films (M_w = 1.48–1.63 × 10^5 g mol^{-1}, M_w/M_n = 1.75–1.89) were similar to those of the pure PLLA film (M_w = 1.63 × 10^5 g mol^{-1}, M_w/M_n = 1.83), meaning that the addition of TiO$_2$ particles did not enhance thermal degradation of PLLA during the molding process. Melting, crystallization, and glass transition temperatures (T_m, T_c, and T_g, respectively) and enthalpy of melting and crystallization (ΔH_m and ΔH_c, respectively) of the films were determined by a Shimadzu DSC-60 differential scanning calorimeter (DSC). The measurements were performed from 0 to 220°C under a nitrogen gas flow at a rate of 10°C/min using about 8 mg of samples. T_m, T_c, T_g, ΔH_m, and ΔH_c were calibrated using indium as a standard. The χ_c values of the PLLA composite films were calculated according to the following equation:

$$\chi_c \,(\%) = 100 \times (\Delta H_m + \Delta H_c)/(X_{PLLA} \times 135)$$

where 135 (J/g of polymer) is the enthalpy of fusion of PLLA crystals having infinite crystal thickness reported by Miyata and Masuko.[24] By definition, ΔH_m and ΔH_c are positive and negative, respectively. The mechanical properties of the films were measured at 23°C and 50% relative humidity using a DCS-5000 AUTOGRAPH (Shimadzu Co., Kyoto, Japan) at a cross-head speed of 5 mm/min. The initial gauge length was kept at 30 mm. The surface of PLLA films

TABLE II
Thermal Properties of the Pure PLLA and the Composite Films with 55A, 55C, D-2, and KA10C

Additive	Content of TiO$_2$ (wt %)	T_m (°C)	T_c (°C)	T_g (°C)
No	0	172	97	57
55A	2	172	96	57
	5	172	93	56
	10	171	93	56
	20	172	91	57
	30	172	90	56
55C	2	172	95	57
	5	172	95	57
	10	172	92	57
	20	172	83	58
	30	171	80	56
D-2	2	171	95	58
	5	171	93	58
	10	171	92	57
	20	171	85	58
	30	171	82	59
KA10C	2	172	98	57
	5	172	97	55
	10	172	97	55
	20	172	98	55
	30	171	98	54

before and after enzymatic hydrolysis was observed by a model S-4500 field emission scanning electron microscope (Hitachi Co., Tokyo, Japan).

RESULTS AND DISCUSSION

Thermal properties

The thermal properties of the pure PLLA and the composite films containing TiO$_2$ before hydrolysis are listed in Table II, which were determined from the DSC thermograms. The previous study indicated that the composite films with CaCO$_3$ as well as the pure PLLA films prepared by quenching from the melt were in an amorphous state.[18] The χ_c of the composite films with TiO$_2$ was 0%, indicating that the films were also in an amorphous state after melt-quenching (data not shown). The hydrophobic TiO$_2$ surface treated with stearic acid such as 55C and D-2 induced the drop in T_c of PLLA without significant changes of both T_g and T_m of PLLA. The T_c values decreased with the content of TiO$_2$ from 97°C at 0 wt % to ~ 80°C at 30 wt %, suggesting that TiO$_2$ surface treated with stearic acid enhanced nucleation of PLLA crystallites. In contrast, the T_c values of the PLLA composite films with CaCO$_3$ were greater than that of the pure PLLA film.[18] On the other hand, the hydrophilic TiO$_2$ without surface treatment such as KA10C led to no significant changes of T_g, T_c, and T_m of PLLA at any content, which implies that the interaction between the particles and PLLA in the composite was very weak or insignificant. The hydrophilic TiO$_2$ surface treated
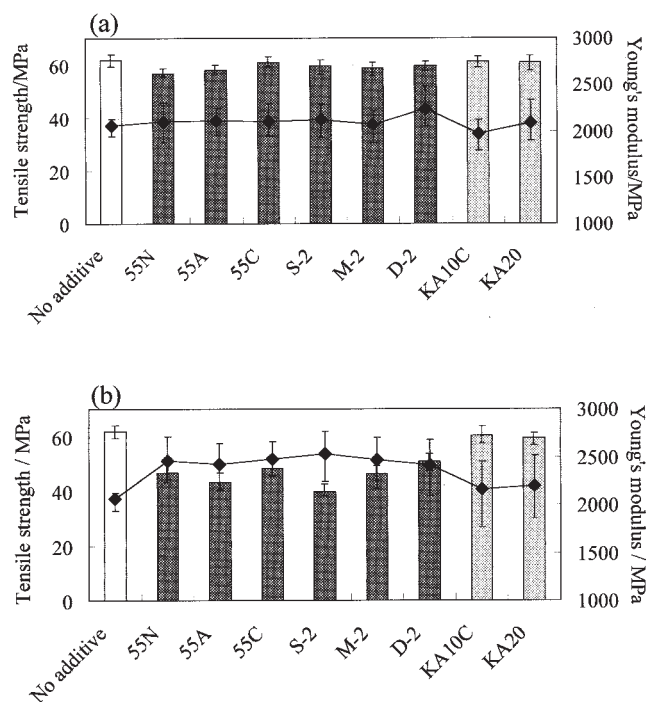
Figure 1 Tensile strength (bars) and Young's modulus (dots) of the pure PLLA and the composite films with 5 wt % (a) and 20 wt % (b) of different TiO$_2$. □ no additive; ▨ rutile-type TiO$_2$; ▧ anatase-type TiO$_2$.

with Al$_2$O$_3$, 55A, induced the modest drop in T_c of PLLA to 90°C at 30 wt %.

Mechanical properties

Tensile strength and Young's modulus of the composite films containing 5 and 20 wt % of different TiO$_2$ particles, together with those of the pure PLLA film, are shown in Figures 1(a) and (b), respectively. No remarkable changes in both the tensile strength and Young's modulus were observed for all the composite films containing 5 wt % of TiO$_2$ particles [Fig. 1 (a)]. However, as seen in Figure 1(b), the tensile strength of the composite films excluding those with KA10C and KA20 was lowered and the Young's modulus became higher with increasing the content of TiO$_2$ particles, indicating that the tensile properties depend mainly on the content of TiO$_2$. This was in agreement with results of PLLA–smectite clay composites prepared by solvent-cast blending[25] and PLLA–CaCO$_3$ composites,[18] but in contrast with those of PLLA-layered silicate nanocomposite prepared by melt extrusion,[26] in which increases in flexural strength were observed at around an additive amount of 4 wt %. The tensile strength and Young's modulus of the composite films containing 20 wt % of S-2, M-2, and D-2 (particle size: S-2 < M-2 < D-2) increased and decreased in this order, respectively, suggesting that TiO$_2$ particles with

a smaller size have a stronger tendency to induce the drop in the tensile strength and the rise in the Young's modulus. The tensile strength of the composite films containing 20 wt % of KA10C and KA20, with a mean particle size of 0.3–0.5 μm, was comparable to that of the pure PLLA film and was superior to that of the films with 20 wt % of TiO$_2$ particles with a mean particle size of < 0.1 μm such as 55N, 55A, 55C, and S-2 [Fig. 1(b)]. These results indicate that the tensile properties depend on the size of TiO$_2$ particles at relatively high contents such as 20 wt %.

The tensile strength and Young's modulus of the composite films containing rutile-type 55N, 55A, and 55C, which are nontreated, Al$_2$O$_3$ treated, and Al$_2$O$_3$-stearic acid treated, respectively, exhibited no remarkable differences. This suggests that the tensile properties are not appreciably dependent on the surface treatment. The assumption is also supported by no significant difference in the tensile strength between the composite films containing 20 wt % of KA10C and KA20, which are anatase-type TiO$_2$ particles without surface treatment and with Al$_2$O$_3$ treatment, respectively.

Enzymatic hydrolysis

The typical nonnormalized weight loss of the films during the enzymatic hydrolysis in the presence of proteinase K is plotted in Figure 2 as a function of hydrolysis time. The nonnormalized weight loss is due to the hydrolyzed PLLA and the released TiO$_2$. The weight loss of the pure PLLA and the composite films increased linearly with time without any induc-
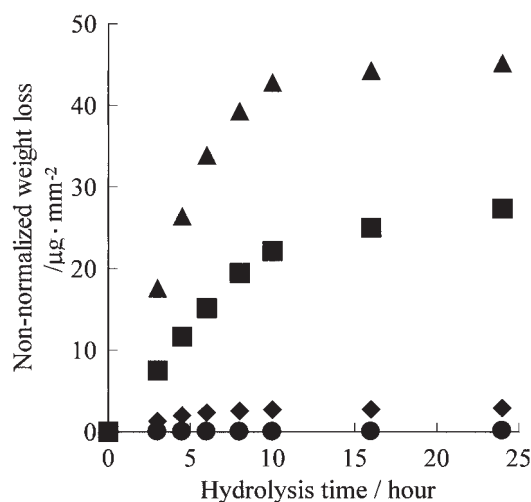

Figure 2 Nonnormalized weight losses per unit surface area of the pure PLLA (■) and the composite films with 20 wt % of D-2 (◆) and KA10C (▲) as a function of enzymatic hydrolysis time, together with weight loss of PLLA composite film with 20 wt % of KA10C in the solution without proteinase K (●).

TABLE III
Dependence of the Nonnormalized Weight Losses of the Pure PLLA and the Composite Films with 20 wt % of Different TiO$_2$ by the Enzymatic Hydrolysis on the Film Thickness

		Weight loss			
		wt %		μg/mm^2	
Additive	Film thickness (μm)	3 hours	4.5 hours	3 hours	4.5 hours
No	150	8.3	12.8	7.4	11.5
	300	4.4	6.8	7.5	11.7
55A	150	9.0	13.4	9.1	13.6
	300	4.9	7.1	9.6	14.1
55C	150	4.4	6.5	4.4	6.6
	300	2.2	3.3	4.2	6.4
D-2	150	1.6	2.4	1.7	2.4
	300	0.7	1.0	1.3	2.0
KA10C	150	16.7	25.0	17.4	26.0
	300	8.7	13.1	17.6	26.4

tion periods for the hydrolysis period of 0–4.5 h. The weight loss rates of the film in the period of 0–4.5 h became higher upon the addition of 20 wt % of KA10C, while the addition of 20 wt % of D-2 hindered markedly the hydrolysis of the film. The weight loss rates for both the pure PLLA and the composite films slowed down gradually in the period of 4.5–24 h, which would be ascribed to the deactivation of proteinase K arising from the labile higher-order structure in the solution and/or to deviation of the pH value giving optimal activity due to formation of a large amount of L-lactic acid. The weight losses of both the pure PLLA and the composite films were negligible in the Tris–HCl buffer without proteinase K, indicating that the weight loss is triggered solely by the enzymatic hydrolysis of PLLA in the presence of proteinase K and the subsequent release of TiO$_2$ particles into the surrounding media.

The nonnormalized weight losses of the pure PLLA and the composite films with 20 wt % of different TiO$_2$ with 150 and 300 μm thickness are tabulated in Table III. The weight losses of the thinner films (150 μm) were greater than those of the thicker ones (300 μm) when the enzymatic hydrolysis was evaluated on the basis of the whole film weight (wt %). On the other hand, almost the same weight losses were observed for the films of both thicknesses when assessed based on the unit surface area. These results reveal that these films have been enzymatically hydrolyzed via a surface erosion mechanism in agreement with reported results,[16] although two modes of bulk erosion and surface erosion have been proposed as a general hydrolysis mechanism of PLLA.[27–31]

The nonnormalized and normalized weight loss rates of the pure PLLA and the composite films containing 20 wt % of different TiO$_2$ particles during the enzymatic hydrolysis are presented in Table IV. The normalized weight loss depends solely on the hydrolyzed PLLA. Here, the weight loss rates were calcu-

lated from the slope of the weight loss lines for the hydrolysis period of 0–3 h. The nonnormalized weight loss rates of the composite films containing hydrophilic TiO$_2$ particles without surface treatment, such as 55N and KA10C, and those surface-treated with only Al$_2$O$_3$, such as 55A and KA20, were in the range 3.1–5.9 μg/mm^2 h, and the normalized weight loss rates were in the range 2.6–5.0 μg/mm^2 h, indicating that the weight loss rates of the composite films are higher than 2.5 μg/mm^2 h of pure PLLA film. The enhancement would be due to the enzymatic hydrolysis at the interfaces between the PLLA matrix and the hydrophilic TiO$_2$ particles as well as on the film surface, as a result of the facile permeation of the enzyme into the interfaces as these TiO$_2$ particles are hydrophilic. Such enzymatic hydrolysis at the interfaces between PLLA matrix and additive materials has been reported for PLLA/CaCO$_3$,[18] PLLA/poly-(ε-caprolactone),[32,33] and PLLA/poly(vinyl alcohol) blends.[34] The increases in the rates for the composite films with KA10C and KA20, which have a particle size of 0.3–0.5 μm, were much greater than those for

TABLE IV
Nonnormalized and Normalized Weight Loss Rates of the Pure PLLA and the Composite Films with 20 wt % of Different TiO$_2$ during the Enzymatic Hydrolysis

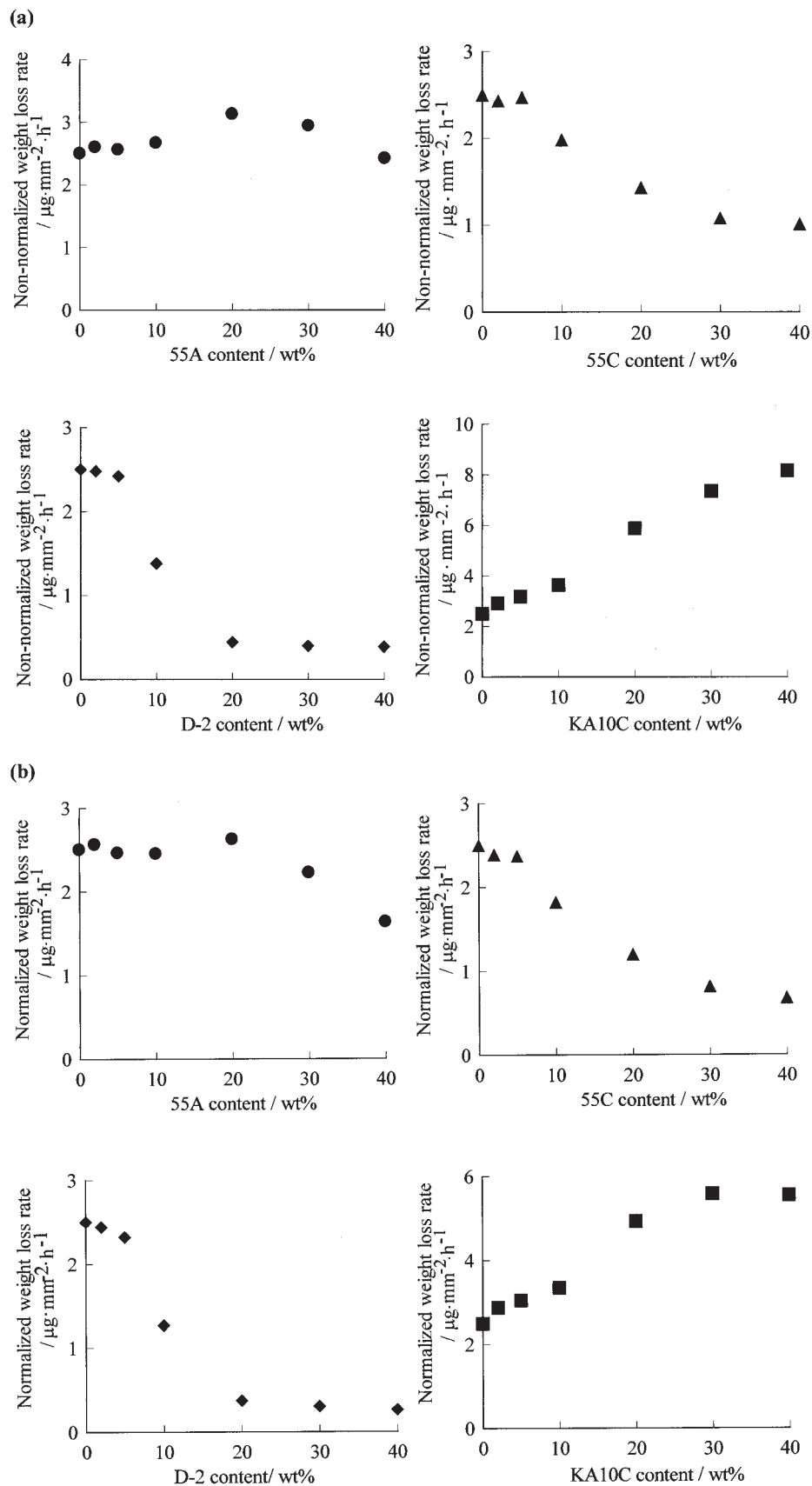| Added TiO$_2$	Nonnormalized weight loss rate (μg mm^{-2} h^{-1})	Normalized weight loss rate (μg mm^{-2} h^{-1})
No additive	2.50	2.50
55N	3.11	2.61
55A	3.13	2.63
55C	1.43	1.20
S-2	0.56	0.47
M-2	0.49	0.41
D-2	0.45	0.37
KA10C	5.87	4.93
KA20	4.96	4.17

Figure 3 Nonnormalized (a) and normalized (b) weight loss rates of PLLA composite films with 55A, 55C, D-2, and KA10C during the enzymatic hydrolysis as a function of TiO₂ content.
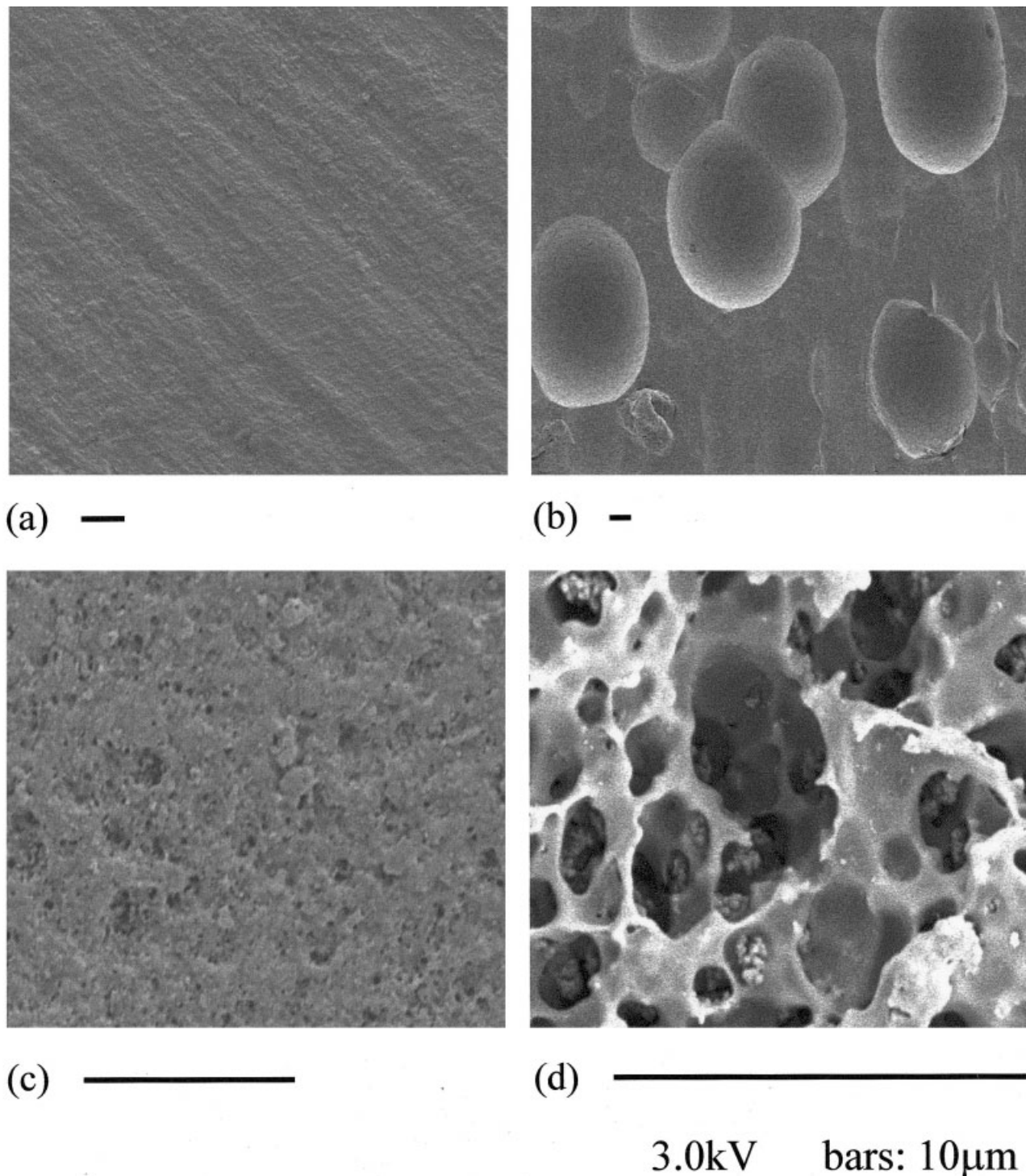
3.0kV   bars: 10μm

Figure 4 SEM photographs of the pure PLLA films (a and b) and the composite films with 20 wt % of D-2 (c) and KA10C (d) before (a) and after (b–d) enzymatic hydrolysis for 48 h.

the composite films with 55A and 55N, which have a particle size of 0.03–0.05 μm, indicating that hydrophilic TiO$_2$ particles having particle sizes of the order of submicron are more effective for the enhancement of the weight loss rates.

The nonnormalized weight loss rates of the composite films containing hydrophobic TiO$_2$ particles sur-

face treated with stearic acid such as 55C, S-2, M-2, and D-2 were in the range 0.4–1.5 μg/mm^2 h, and the normalized weight loss rates were in the range 0.3–1.2 μg/mm^2 h, indicating that the enzymatic hydrolysis of PLLA was inhibited by the presence of the hydrophobic TiO$_2$ particles. Probably, the hydrophobic surface treatment of TiO$_2$ particles inhibited the access of
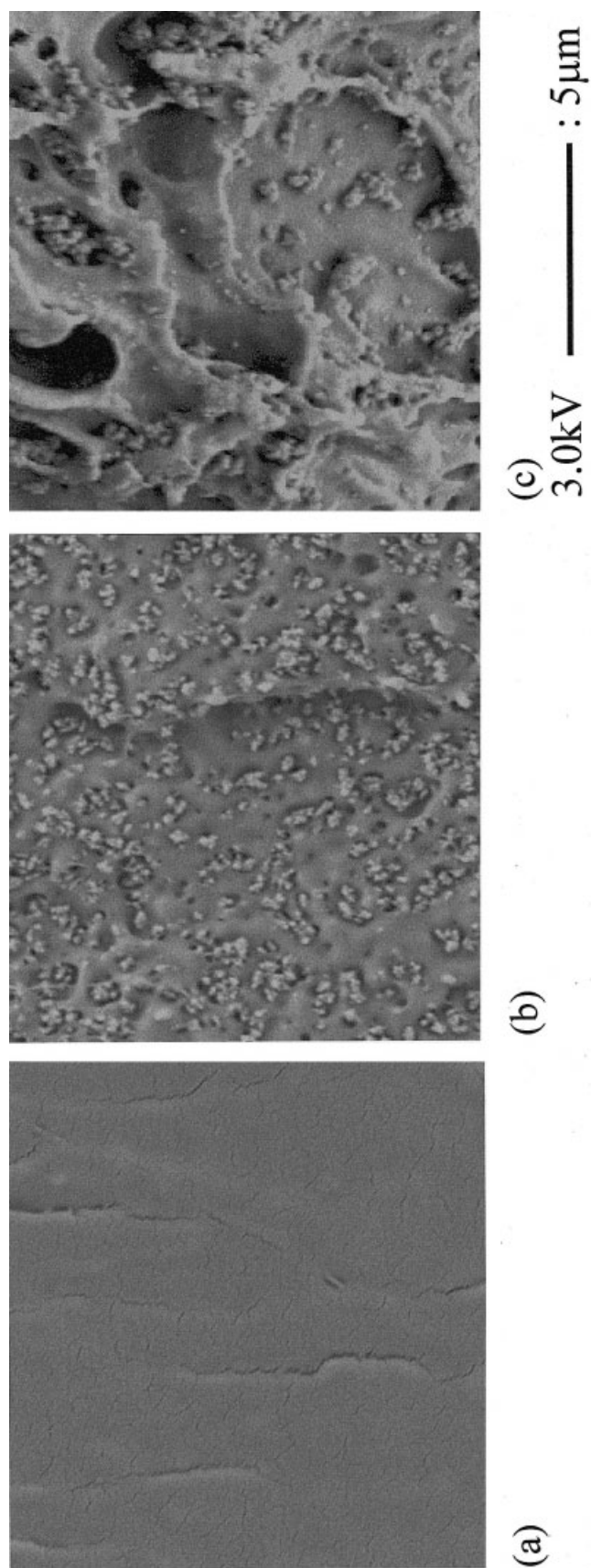
Figure 5 SEM photographs of the freeze-fractured surfaces of the pure PLLA (a) and the composite films with 20 wt % of D-2 (b) and KA10C (c) after enzymatic hydrolysis. The fractured surfaces of ~ 40–50 μm in depth from the outer surface were observed.

proteinase K to the interface between PLLA and the particles and/or the hydrophobic acid released from the particles diffused into the PLLA matrix and thereby disturbed the adsorption of proteinase K to the matrix. Since the enzymatic hydrolysis of PLLA was accelerated by low contents (5–10 wt %) of hydrophobic $CaCO_3$ particles surface treated with stearic acid and palmitic acid,[18] the results with hydrophobic TiO_2 particles seem to be in conflict with those with hydrophobic $CaCO_3$ particles. This may suggest that the enzymatic hydrolysis of PLLA in the composites with the TiO_2 particles is more susceptible to the hydrophilicity of the films compared with composites with $CaCO_3$ particles.

The nonnormalized and normalized weight loss rates of the composite films containing 55A, 55C, D-2, and KA10C during the enzymatic hydrolysis are plotted as a function of TiO_2 content in Figure 3(a) and (b), respectively. Interestingly, the weight loss behavior during the hydrolysis depended upon the type of added TiO_2 particles, in contrast to those for the composite films with $CaCO_3$ particles, all of which accelerated the enzymatic hydrolysis at contents less than 10 wt % and led to a drop in the enzymatic hydrolysis rates at the higher contents.[18] The addition of 55A at contents from 2 to 40 wt % led to no remarkable change of nonnormalized weight loss rates. The addition of 55C and D-2 decreased monotonically the nonnormalized and normalized weight loss rates of the composite films. At a content of 40 wt %, their nonnormalized weight loss rates were 40 and 16% of initial values and their normalized weight loss rates were 27 and 10% of initial values, respectively. On the other hand, the composite films with KA10C exhibited the monotonous increase of the nonnormalized and normalized weight loss rates with increasing contents of KA10C to 8.16 and 5.54 $\mu g \cdot mm^{-2} \cdot h^{-1}$ at 40 wt %, respectively. This acceleration was greater than that for the PLLA composite films with any $CaCO_3$.[18] These results suggest that the hydrolyzability of the PLLA can be controlled in a wide range by altering the type and amount of the added TiO_2 particles.

Morphology

SEM photographs of the surfaces of the pure PLLA and the composite films with 20 wt % of D-2 and KA10C before and after enzymatic hydrolysis for 48 h are shown in Figure 4. The surfaces of these films were all smooth before enzymatic hydrolysis, as illustrated in Figure 4(a) for the pure PLLA film. After hydrolysis, many pores with diameters of 30–60 μm were formed on the surfaces of the pure PLLA film [Fig. 4(b)]. The surface of the composite film with 20 wt % of D-2 appeared somewhat smooth even after the hydrolysis with the presence of many tiny pores [Fig. 4(c)], reflecting the very low hydrolyzability of the composite

films with D-2, as seen in Table IV and Figure 3. In contrast, many pores, along with granules of KA10C, were observed for the surface of the composite film with 20 wt % of KA10C after the hydrolysis [Fig. 4 (d)]. The density of the pores was much higher than that on the surface of the pure PLLA film, reflecting that the enzymatic hydrolysis of PLLA was accelerated by the addition of KA10C.

SEM photographs for the surface of the freeze-fracture using liquid nitrogen of the pure PLLA and the composite films with 20 wt % of D-2 and KA10C after enzymatic hydrolysis for 48 h are shown in Figure 5. The three fractured surfaces at ∼ 40–50 μm from the outer surface quite differed from one another. However, no traces of enzymatic hydrolysis were observed for all the fractured surfaces, implying that the hydrolysis of these films arises from the film surface. This result supports the fact that the enzymatic hydrolysis proceeds via the surface erosion mechanism, which is shown in Table III.

CONCLUSION

The tensile strength of the PLLA composite films with TiO_2 particles was lowered and the Young's modulus became higher with increasing the content of TiO_2 particles excluding anatase-type ones, irrespective of the surface treatment. The weight loss rates of PLLA matrix during the enzymatic hydrolysis in the presence of proteinase K increased and decreased upon composite formation with hydrophilic anatase-type TiO_2 particles with a mean particle size of 0.3–0.5 μm and hydrophobic rutile-type TiO_2, respectively. The mechanical properties and enzymatic hydrolyzability of the PLLA could be controlled by the type and amount of the added TiO_2 particles.

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