New Chitin-Based Polymer Hybrids, 4: Soil Burial Degradation Behavior of Poly(vinyl alcohol)/Chitin Derivative Miscible Blends

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ABSTRACT: Soil burial degradation behavior of miscible blend systems of poly(vinyl alcohol) (PVA)/partially deacetylated chitin (1), PVA/chitin-graft-poly(2-methyl-2-oxazoline) (2), and PVA/chitin-graft-poly(2-ethyl-2-oxazoline) (3) was investigated in comparison with the case of a pure PVA film. The degradation of the blend films was followed by the weight changes, scanning electron microscopic observation, Fourier transform infrared spectroscopy, ¹H-NMR, and size exclusion chromatography analyses. The rate of weight decrease in these PVA/chitin derivative hybrids was higher than that of control PVA in the soil burial test. Fourier transform infrared spectra of the recovered samples of the blends showed an apparent increase of the absorption intensity due to β -diketone structure in PVA, which reflects the progress of biodegradation of PVA by PVA-oxidizing enzymes. Scanning electron microscopic observation revealed that these blend films were degraded by bacteria and actinomycetes. The triad tacticity and number-average molecular weight of PVA in the hybrids after soil burial determined by ¹H-NMR and size exclusion chromatography, respectively, were almost the same as those before soil burial. These results suggested that enzymatic degradation of the hybrid films occurred mainly on the surface and that degradation of the PVA-based samples in the soil was accelerated by blending the chitin derivatives. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1171-1179, 1999

Key words: biodegradable polymer; miscible blend; chitin; poly(vinyl alcohol) (PVA); poly(2-alkyl-2-oxazoline); graft copolymer

INTRODUCTION

Development of biodegradable polymers is of great importance, because environmental pollution due to plastic wastes has become increasingly serious. Both industrial and academic communities have been making a great effort to develop low-cost, functional, biodegradable polymers. For practical application, the control of biodegradation is an essential subject. To achieve this goal, a new molecular design of biodegradable polymers is one of the possible choices. We have already reported synthesis and degradabilities of novel carbohydrate-based polyesters^{1–3} and related ring-containing polymers.^{4–6} They are derived from renewable natural resources and/or designed so as to comprise essential parts of natural products as repeating units. Biodegradation control of these polyesters has been attained by architectural regulation of the chemical structure.

Another important method to develop degradable materials with a variable degradation rate

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should be blends of biodegradable polymers having different degradabilities. Poly(ethylene oxide)/poly(3-hydroxybutyrate),⁷ poly(vinyl alcohol) (PVA)/poly(3-hydroxybutyrate),⁸ poly(ethyleneco-vinyl alcohol)/starch,⁹ and poly(vinyl acetate)/ poly(lactic acid)¹⁰ have been already reported as miscible or compatible biodegradable blends. In these blend systems, physical properties (thermal properties, wetting of the surface, miscibility, aging, etc.), as well as chemical structure, influence enzymatic erosion.^{9,10} Among synthetic polymers, PVA is the only vinyl-type polymer that has been confirmed to be biodegradable,^{11–14} although its biodegradation rate is too slow for practical utilization as a degradable polymer under natural environmental conditions. Blend of PVA and a suitable biopolymer would be one of the most effective approaches to improve the biodegradability of PVA. We have already reported PVA/ chitin-graft-poly(2-alkyl-2-oxazoline)¹⁵⁻¹⁷ and PVA/polv(sodium $\alpha.\beta$ -D.L-aspartate)¹⁸ blends as miscible pairs.

As a biodegradable and biocompatible polysaccharide, chitin is one of the most abundant structural biopolymers, which mainly consists of Nacetyl-D-glucosamine units. Chitin is rapidly hydrolyzed by biological degradation processes, although it is highly resistant to chemical and physical degradation. Thus, its actual utilization is restricted owing to the low solubility and compatibility that are ascribed to its strong crystalline structure. Proper derivatization of chitin is a key to a wide range of its applications to biomedical and biodegradable materials.^{19–22} We have already reported the synthesis of chitin derivatives having monodisperse²³ poly(2-alkyl-2-oxazoline) [i.e., chitin-graft-poly(2-methyl-2-oxazoline) (2) and chitin-graft-poly(2-ethyl-2-oxazoline) (3)] by the reaction of partially deacetylated chitin (1)with living poly(2-methyl-2-oxazoline) and poly(2ethyl-2-oxazoline), respectively.^{24,25} Poly(2-alkvl-2-oxazoline)s, which are produced by the ringopening isomerization polymerization of 2-alkyl-2-oxazolines, have been shown to possess a low toxicity²⁶ and a high miscibility with various commodity polymers.^{15,16,27} These chitin derivatives showed much improved solubilities in several organic solvents and much improved miscibility with PVA¹⁵⁻¹⁷ and poly(vinyl chloride),^{16,28,29} compared with chitin or deacetylated chitin. Recently, Naka and colleagues³⁰ have reported that the graft copolymer 2 interacts with lipase and catalase to stabilize enzymatic functions.

This article is concerned with soil burial degradation behavior of chitin-based polymer hybrids, PVA/partially deacetylated chitin (1),^{15,31} PVA/ graft copolymer **2**,^{15,16} and PVA/graft copolymer **3**¹⁷ miscible blend systems and the relationship between the degradation rate and physical properties. Degradation study of miscible chitinous blends has not been hitherto reported to our knowledge, because miscibility of chitin or its derivatives is generally too low to form miscible polymer blends.

EXPERIMENTAL

Materials

Chitin from crab shells was purchased from Sigma Chemical Co. (St. Louis). Partially deacetylated chitin (1) with ~ 50% N-deacetylation was prepared by the method of Sannan and colleagues.³² Chitingraft-poly(2-methyl-2-oxazoline) (2) and chitingraft-poly(2-ethyl-2-oxazoline) (3) were synthesized according to the literature.^{24,25} Commercially available PVA ($M_n = 88,000$; Nacalai Tesque, Inc.) was used for hybrid films. Dimethyl sulfoxide- d_6 (Aldrich Chemical Co.) was used without purification for NMR analysis. Solvents used were purified by distillation.

Instruments and Measurements

Differential scanning calorimetry (DSC) of dried films (9-13 mg) was conducted with a Perkin-Elmer DSC-2 (calibration: indium and tin; heating rate: 5°C min⁻¹). To provide the same thermal history for all samples, thermal properties for the blends were measured after one heating cycle to 110°C, followed by quenching to 20°C in DSC. The glass transition temperature (T_g) and melting temperature (T_m) were determined at the inflection point of the specific heat increment and the onset of the endothermic peaks of DSC traces, respectively. Tensile strength of the blend films was evaluated with cast films of 40 mm imes 5 mm imes 0.04 mm specimens with a Shinkoh TCM-500 testing machine with extension rate of 20 mm min^{-1} at room temperature (relative humidity: 50%). Tensile strength values listed in the text are the mean of 5–9 samples. Contact angles against water were measured at room temperature with a CAD-type goniometer (Kyowa Co., CA-DT). The contact angle of each film sample was measured on at least 15 spots, and the values were averaged. ¹H-NMR spectra were recorded on a Bruker ARX 400 Fourier

								Hydroph	ilicity		
Chitin	Chitin DAª	Po	oly(2-oxa (PRO2	,	[PROZO] ^d	$M_n^{\rm e}$	T f	Solubility ^g	Contact Angle ^h	Miso	vibility with PVA
Derivative	(%)	R	n^{b}	$M_w/M_n^{ m c}$	$[NH_2]$	$(\times 10^{-5})$	$T_g^{\rm f}$ (°C)	(mg mL^{-1})	(°)	k^{i}	
1 2a 2b	$52 \\ 52 \\ 52$	 Me	 19.6 32.8	 1.1_3 1.1_2	$1.00 \\ 0.45$	0.72 3.9 9.8	 66 66	$5\\44\\38$	$72 \\ 14 \\ 23$	$0.21^{\rm k}$ $0.25^{\rm k}$	Miscible ^j Miscible ^k Miscible ^k
3	45	Et	21.7	$1.1_2 \\ 1.1_2$	0.95	5.9	36	44	42	$0.20 \\ 0.04^{1}$	Compatible ¹

Table I Characterization of Chitin Derivatives (1-3)

^a Degree of N-acetylation of deacetylated chitin, by ¹H-NMR in D₂O/CD₃COOD (95 : 5, v/v).

^b DP of the side chain, ¹H-NMR in CDCl₃ at 27°C.

^c By SEC in CHCl₃ (polystyrene standard).

^d Molar ratio of poly(2-oxazoline) (PROZO) unit to D-glucosamine unit of 1, by ¹H-NMR.

^e By SEC in H₂O (pullulan standard).

^f By DSC.

^g Solubility in H₂O at 27°C.

^h Contact angle against H₂O of the air side surface in the film at room temperature.

ⁱ k from Gordon–Taylor equation (ref. 35).

^j Refs. 15 and 31.

^k Ref. 16.

¹ Ref. 17.

transform (FT) NMR spectrometer operating at 400 MHz. Infrared (IR) spectra were measured on a JASCO FT/IR-610 spectrophotometer. Microsampling FT-IR spectra were taken by a JASCO FT/IR-610 spectrophotometer with a JASCO MICRO-20 IR microscope. Surfaces of the films after soil burial tests were observed with Hitachi S-2150 and S-4500 scanning electron microscopes (SEMs). Fractured surfaces of the recovered films were also observed with a Hitachi S-4500 SEM. To prepare samples for fractured SEMs, the blend films were embedded in epoxy resin (Ouken Co., Ltd., EPON 812) at 35°-60°C for 5 days. Embedded blends were cut and sputter-coated with platinum palladium. The M_n and M_{w}/M_{n} values of samples were determined by size exclusion chromatography (SEC) (temperature: 27°C; column, Shodex B804 + 805; eluent, 0.03M phosphate buffer; pH 7.2; flow rate, 1.0 mL min^{-1}). The SEC system was calibrated with poly(ethylene oxide) standards (Tosoh Co. Ltd.).

Solubility of Chitin Derivatives in Water

A chitin derivative (100 mg) was dissolved in 2 mL of water at 27°C for 24 h. After stirring, the aqueous solution was filtered with a disposable syringe filter unit (Advantec Co. Ltd., DISMIC-25cs; 0.80 μ m). The filtrate was lyophilized, and the weight of the powder was measured to evaluate the solubility in water (mg mL⁻¹).

Preparation of Miscible Blend Films by the Solvent Cast Method

According to our previous reports,^{15–17} 70 mg of PVA was dissolved in 10 mL of water at 120°C in an autoclave. After cooling at room temperature, chitin/poly(2-methyl-2-oxazoline) graft copolymer **2a** (30 mg; structure is shown in Table I) was added to the solution. The solution was placed on a Teflon laboratory dish (50 mm diameter) at 50°C to evaporate the solvent. The film was further dried *in vacuo* at 50°C for 3 days. Removal of water was confirmed by thermogravimetric measurement. Thickness of the film was 40 μ m.

Soil Burial Degradation

Thin films of 20 mm \times 10 mm \times 0.04 mm size of PVA/chitin derivative blends and control PVA were buried in soil, which had been composted for > 10 years in Nagoya University Farm (pH 7.1–7.4). They were kept in an atmosphere controlled at 70–80% relative humidity at 27°C. After several months, the films were taken out and washed in diethyl ether to remove the soil. Samples were dried to constant weight under reduced pressure, and the weights of the recovered hybrids were determined.

Radical Oxidation of PVA

As a model compound of an intermediate in the biodegradation process of PVA, radically oxidized

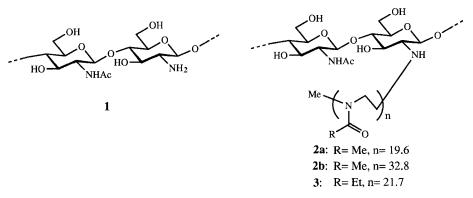


Figure 1 Chemical structures of partially deacetylated chitin (1), chitin-*graft*-poly(2-methyl-2-oxazoline) (2), and chitin-*graft*-poly(2-ethyl-2-oxazoline) (3).

PVA was prepared according to the literature.^{33,34} After 50 mL of an aqueous solution of PVA (500 mg, 11.4 mmol) and ammonium persulfate (300 mg, 1.32 mmol) were stirred at 60°C for 5 h, the reaction mixture was poured into 1 L of methanol to precipitate a polymer. White powdery oxidized PVA was obtained by reprecipitation from water to methanol twice and dried *in vacuo*. The yield was 86.0%.

RESULTS AND DISCUSSION

Characterization of Chitin Derivatives

Chemical structure and characterization data of partially deacetylated chitin (1), chitin-graftpoly(2-methyl-2-oxazoline) (2), and chitin-graftpoly(2-ethyl-2-oxazoline) (3) are shown in Figure 1 and Table I. The main chain of chitin derivatives 1–3 was all randomly $\sim 50\%$ deacetylated.³² Poly(2-alkyl-2-oxazoline) (PROZO) branches of graft copolymers 2 and 3, which exhibit miscibility with PVA,^{15,17} were attached to the 2-position of the D-glucosamine units of the main chain. The side chain length was regulated by living polymerization of 2-alkyl-2-oxazoline in acetonitrile. The [PROZO]/[-NH₂] values in Table I represent the molar ratios of oxazoline polymer to D-glucosamine units in 2 and 3, determined by 1 H-NMR signal intensity ratios of H-1 proton of Dglucosamine unit (δ 4.89 ppm) to terminal Nmethyl proton of poly(2-methyl-2-oxazoline) segment (§ 3.12-2.80 ppm) and H-1 proton of D-glucosamine unit (δ 4.91 ppm) to terminal Nmethyl proton of poly(2-ethyl-2-oxazoline) segment (δ 3.05–2.91 ppm), respectively. As confirmed by DSC analysis, samples 1-3 were all

amorphous polymer. Graft copolymers 2 and 3 had a T_{σ} at 66°C and 36°C, respectively, whereas no glass transition of 1 was observed up to 240°C. Graft copolymers 2 and 3 had better solubility in water $(38-44 \text{ mg mL}^{-1})$ than graft copolymer 1 (5 mg mL⁻¹). Introduction of poly(2-oxazoline) segment to chitin is effective in the preparation of chitinous blend films by solvent casting from an aqueous solution. Miscibilities of the chitin derivatives with PVA have been demonstrated by DSC and FT-IR analyses in our previous reports.^{15–17} The interaction of chitin derivatives with PVA was evaluated by k value from the Gordon–Taylor $plot^{35}$ in the blend. The large k value indicates the strong interaction of PVA with the chitin derivative, in the range of k < 1. In PVA/chitin-graftpoly(2-alkyl-2-oxazoline) blends, miscibility in the blend is roughly controlled by changing the number, chain length, and alkyl group of the poly(2alkyl-2-oxazoline) branches introduced in the graft copolymer.^{16,17} The k value of 2a (0.21)¹⁶ was lower than that of 2b (0.25),¹⁶ but considerably higher than that of $\mathbf{3}$ (0.04).¹⁷

Characterization of PVA/Chitin Derivative Blend Films

Table II summarizes the thermal and mechanical properties of PVA/chitin derivative blend films and their surface characteristics evaluated by the contact angle measurement against water. The PVA film had a T_g at 72°C and a T_m at 212°C. By blending 1 with PVA, T_g of PVA increased and T_m of PVA decreased. On the other hand, blends of PVA with 2 and 3 showed the depressions of both T_g and T_m . The depressions indicate an increased mobility of PVA segment, which might promote the biodegradation. The PVA/3 blend has rela-

Sample	$T_g^{\ b}$ (°C)	$T_m^{\ c}$ (°C)	Tensile Strength ^d (MPa)	Contact Angle ^e (°)
PVA	72	212	87	66
PVA/1 (30 wt %)	117	211	38	71
PVA/2a (20 wt %)	68	212	82	39
PVA/2a (30 wt %)	68	206	40	33
PVA/ 2b (30 wt %)	69	201	34	46
PVA/3 (10 wt %)	47	208	86	61
PVA/3 (20 wt %)	42	206	81	50
PVA/3 (30 wt %)	42	205	61	49

Table IICharacterization of PVA/ChitinDerivative Blend Films^a

 $^{\rm a}$ Prepared by the solvent cast method from an aqueous solution on a Teflon plate (film thickness: 40 μm). Cf. refs. 16 and 17.

^b Glass transition temperature, by DSC.

^c Melting point, by DSC.

^d Measured at room temperature (relative humidity: 50%). ^e The surface of the air side, measured at room temperature.

tively lower T_g among these blends, which is ascribed to lower T_g of the blend component, graft copolymer **3** (vide supra).

The tensile strength of PVA was 87 MPa, in agreement with the literature value (84 MPa).³⁶ Although a reinforcing effect of mechanical property was not found for the PVA/chitin derivative blends without drawing, the tensile strength of these blends was comparable with that of PVA, despite T_m depressions. For example, the tensile strength values of the PVA/2a (20 wt %) and PVA/3 (20 wt %) blends were 82 and 81 MPa. Presumably, this is caused by the specific intermolecular interaction between chitin derivatives with PVA. Contact angle measurement against water revealed that the surfaces of PVA became more hydrophilic by blending with chitin derivatives 2 or 3. The surface of the PVA/2a blend showed the highest hydrophilicity, probably because of the higher hygroscopic character of **2a** as indicated by the lower water contact angle (Table II).

Degradation Behavior of PVA/Chitin Derivative Blend Films in the Soil

As chitin-based polymer hybrids, PVA/partially deacetylated chitin (1), PVA/chitin-graft-poly(2methyl-2-oxazoline) (2), and PVA/chitin-graftpoly(2-ethyl-2-oxazoline) (3) miscible blend systems were used for soil burial degradation tests. The degradation test was conducted in soil (pH 7.1, 27°C) by monitoring the weights of recovered

chitin-based polymer hybrids and control PVA films. The results of the soil burial tests of PVA/1 (30 wt %), PVA/2a (30 wt %), and PVA/2b (30 wt %) blends are shown in Figure 2. The weight of the recovered hybrids was found to decrease with the burial time. After 150 days, 24 wt % of PVA/1, 11 wt % of PVA/2a, and 47 wt % of PVA/2b blends were recovered. On the other hand, the control PVA film was scarcely degraded (the recovered polymer: 89 wt %) and the shape of the PVA film did not change after 150 days. These results clearly indicate that the chitin derivative-containing hybrid films undergo degradation more rapidly than the control PVA film. The weight decrease of the PVA/2a blend was the fastest among the three blends. Rapid degradation of PVA/2a blend observed in the course of the test during 90-150 days after soil burial seems to be partly due to inevitable mechanical loss of sample specimens below a millimeter scale. The presence of some bacteria was observed on the surface of the PVA/2a (30 wt %) blend film after soil burial for 150 days by SEM measurement. By ¹H-NMR and FT-IR, chitin derivative 2a was not detected in the hybrid film after soil burial for 90 days.

As stated in the Introduction section, PVA is known to have biodegradability. An enzymatic

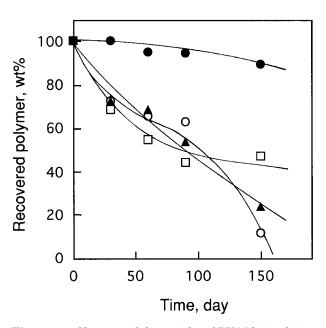


Figure 2 Changes of the weight of PVA/chitin derivative miscible blend films in the soil burial test (pH 7.1, 27°C); \bullet : PVA (control); \blacktriangle : PVA/partially deacetylated chitin (1) (30 wt %); \bigcirc : PVA/chitin-*graft*-poly(2-methyl-2-oxazoline) (2a) (30 wt %); \Box : PVA/chitin-*graft*-poly(2-methyl-2-oxazoline) (2b) (30 wt %).

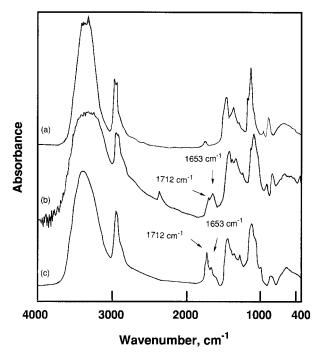


Figure 3 FT-IR spectra of (a) PVA, (b) PVA/chitingraft-poly(2-methyl-2-oxazoline) (**2b**) (30 wt %) after soil burial for 90 days, and (c) radically oxidized PVA.

degradation mechanism of PVA has been already proposed as follows.¹¹⁻¹⁴ Degradation of PVA proceeds by way of β -diketone structures, which are produced by oxidation of PVA with PVA-oxidizing enzymes. Then, the β -diketone form is cleaved by β -diketone hydrolase. PVA degrades during these successive reactions by these two kinds of enzymes. Changes of the chemical structure of the PVA/chitin derivative blends during soil burial tests were followed by FT-IR spectroscopy. The IR spectra of pure PVA and the PVA/2b (30 wt %) blend after soil burial for 90 days are shown in Figure 3, with that of radically oxidized PVA, as a model compound. When the spectrum of radically oxidized PVA is compared with that of PVA, the appearance of absorptions at 1712 cm^{-1} and 1653 cm^{-1} is observed, which are attributable to simple ketone and β -diketone form (enol-type), respectively [Fig. 3(c)]. In the radically oxidized PVA spectrum, the absorption band at 1653 cm^{-1} was smaller than that at 1712 cm^{-1} . On the contrary, the absorption band at 1653 cm^{-1} was larger than that at 1712 cm^{-1} in the spectrum of PVA/2b (30 wt %) after soil burial for 90 days [Fig. 3(b)]. The absorption at 1653 cm^{-1} became more intensive in the spectra of the films buried for 150 days. The preferential generation of β -diketone of hybridized PVA after the soil burial test reflects a biologically selective oxidizing mechanism, not radically random oxidation. The β -diketone content was estimated by the ratios of the absorbance at 1653 cm⁻¹ to that at 2944 cm⁻¹ ($\nu_{\rm C-H}$), as shown in Figure 4. Interestingly, the absorbance ratios A_{1653} ($\nu_{\rm C-O}$)/ A_{2944} ($\nu_{\rm C-H}$) of PVA/**2a** were higher than those of any other blends and control PVA after degradation tests for 150 days, and these results corresponded to the weight changes of the recovered films in the soil burial test (Fig. 2). This suggests an increase in the β -diketone content by enzymatic degradation of the PVA/chitin derivative hybrids, especially the PVA/**2a** blend system, in comparison with the case of the control PVA film.

Triad tacticity of PVA in the PVA/**2a** blend film after soil burial was investigated by using ¹H-NMR spectroscopy in dimethyl sulfoxide- d_6 at 27°C. In the ¹H-NMR spectrum of the original PVA, the proton signals of the hydroxyl groups of isotactic, heterotactic, and syndiotactic triads were observed at 4.67, 4.48, and 4.24 ppm, respectively.³⁷ The triad tacticities are listed in Table III. After the soil burial test of the PVA/**2a** blend for 90 days, the triad tacticity was almost the same as that of the original PVA and of PVA with the same burial time. In contrast, Matsumura

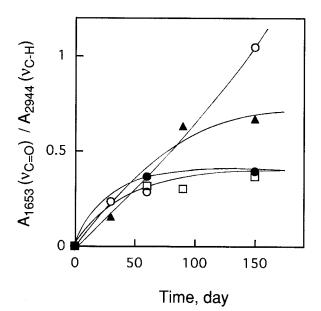


Figure 4 Changes of FT-IR absorbance ratio, A_{1653} ($\nu_{C=O}$)/ A_{2944} ($\nu_{C=H}$), of PVA/chitin derivative miscible blend films in the soil burial test (pH 7.1, 27°C); •: PVA (control); A: PVA/partially deacetylated chitin (1) (30 wt %); \bigcirc : PVA/chitin-graft-poly(2-methyl-2-oxazoline) (2a) (30 wt %); and \Box : PVA/chitin-graft-poly(2-methyl-2-oxazoline) (2b) (30 wt %).

		Tacticity ^b (%)				
Sample	Soil Burial Time (days)	Isotactic	Heterotactic	Syndiotactic		
Control PVA	0	19 ± 1	51 ± 1	30 ± 1		
Control PVA PVA/ 2a	90	21 ± 1	49 ± 2	30 ± 1		
(30 wt %) blend	90	22 ± 5	48 ± 5	30 ± 2		

Table III Tacticity of PVA in PVA/Chitin-*graft*-Poly(2-methyl-2-oxazoline) (2) (30 wt %) Miscible Blend Films before and after Soil Burial for 150 Days^a

^a Film thickness: 40 μm. Conditions of soil burial tests, see Experimental section.

^b Determined by ¹H-NMR spectra in dimethyl sulfoxide-d₆ at 27°C.

and colleagues^{38,39} have reported that the oligomeric isotactic sequence of PVA in a phosphate buffer solution was selectively biodegraded by cell-free extracts of *A. faecalis* KK314, compared with heterotactic and syndiotactic structure.

To clarify the weight loss process, the M_n and M_w/M_n of PVA in the PVA/2 blend film after soil burial were analyzed by SEC using phosphate buffer (pH 7.2) as eluent. The results are listed in Table IV. The recovery of the PVA/2 (30 wt %) blend was 11-47 wt % after soil burial for 150 days (Fig. 2). A slight increase of M_n of PVA in the remaining hybrid after soil burial was found, together with narrower molecular weight distributions. This is ascribed to preferential degradation and disappearance of PVA with relatively low molecular weight. In addition to the stereochemical investigation by ¹H-NMR, SEC analysis indicated that the soil burial degradation of PVA in the hybrid films occurred mainly on the blend surface. This is the reason why the changes in the triad tacticity, M_n , and M_w/M_n indices during the

Table IV Molecular Weight of PVA in PVA/ Chitin-graft-Poly(2-methyl-2-oxazoline) (2) (30 wt %) Miscible Blend Films before and after Soil Burial for 150 Days^a

Sample	Soil Burial Time (days)	$M_n^{ m \ b} imes 10^{-4}$	$M_w/M_n^{ m b}$
Control PVA	0	5.8	1.97
Control PVA	150	6.2	1.9_{4}
PVA/ 2a	150	6.9	1.7_{4}
(30 wt %) blend			-
PVA/ 2b (30 wt %) blend	150	6.8	1.6_{3}

 $^{\rm a}$ Conditions of soil burial tests, see Experimental section. $^{\rm b}$ By SEC in 0.03M phosphate buffer (pH 7.2), poly(ethylene oxide) standard.

present soil burial test are different from those in the enzymatic degradation test (in phosphate buffer, pH 7.2, at 25° C), as reported by Matsumura and colleagues.^{38,39}

Results of the soil burial tests (pH 7.4, 27°C) of PVA/3 (10 wt %), PVA/3 (20 wt %), and PVA/3 (30 wt %) blends are shown in Table V. The weights of the recovered blends decreased with the burial time. After 150 days, 84 wt % of PVA/3 (10 wt %), 50 wt % of PVA/3 (20 wt %), and 51 wt % of PVA/3 (30 wt %) blends were recovered. The degradation rate of PVA/3 (20 wt %) was almost the same as that of PVA/3 (30 wt %).

Moreover, Figure 5 indicates changes in the weight of pure PVA, PVA/2a (20 wt %), and PVA/3 (20 wt %) blend films with the time in the soil burial test (pH 7.4, 27°C). Although graft copolymers 2a and 3 have similar chain length and introduced number of the poly(2-alkyl-2-oxazo-line) branch, the PVA/3 (20 wt %) blend film showed a faster weight decrease than the PVA/2a (20 wt %) blend film. Considering that poly(2-methyl-2-oxazoline) has higher hydrophilicity than poly(2-ethyl-2-oxazoline), it seems likely im-

Table V Weight Loss in Soil Burial of PVA/ Chitin-graft-Poly(2-ethyl-2-oxazoline) (3) Blend Films^a

	Weight Loss (%)				
Sample ^b	After 90 Days	After 150 Days			
PVA	5	5			
PVA/3 (10 wt %)	15	16			
PVA/3 (20 wt %)	29	50			
PVA/3 (30 wt %)	34	49			

 $^{\rm a}\,{\rm The}\,$ soil had been composted (pH: 7.4; temperature: 27°C).

^b Film thickness: 40 μ m.

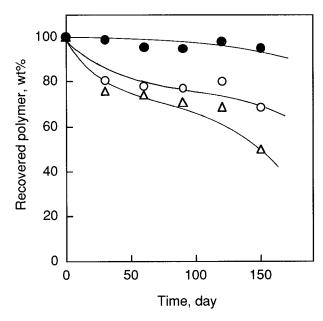


Figure 5 Changes of the weight of PVA/chitin-graftpoly(2-alkyl-2-oxazoline) (20 wt %) blend films in the soil burial test (pH 7.4, 27°C); \bullet : PVA (control); \bigcirc : PVA/chitin-graft-poly(2-methyl-2-oxazoline) (2a) (20 wt %); \triangle : PVA/chitin-graft-poly(2-ethyl-2-oxazoline) (3) (20 wt %).

plied that the higher degradability of the PVA/3 blend is mainly due to the lower T_g and lower intermolecular interaction of the blend components than those of the PVA/2a blend.

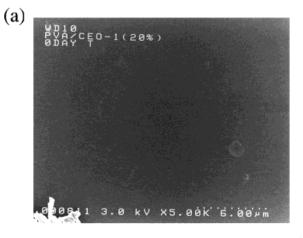
In a microsampling FT-IR surface reflectance spectrum of the degraded part in the PVA/3 (20 wt %) blend film after soil burial test for 120 days, there were absorptions at 1652 ($\nu_{\rm C=O}$) and 1550 ($\nu_{\rm N=H}$) cm⁻¹, which were probably attributable to peptide linkages of some microorganisms adhered to the surface of the film. Peaks were not detected in the normal FT-IR spectrum of the same sample.

Figure 6 shows the SEM photographs of the surface of a PVA/3 (20 wt %) blend film before and after soil burial. On the surface of the film after the soil burial test for 120 days, a number of holes (diameter: $\sim 1.5 \ \mu m$) were observed with bacteria of round shape (diameter: $\sim 0.7 \ \mu m$) [Fig. 6(b)]. The generation of the holes was unambiguously explained by immersion with bacteria. Moreover, the surface was eroded by actinomycetes seen as a branched rod-like form (diameter: $\sim 0.5 \ \mu m$) in the middle of the picture. The results suggest that biodegradation took place on the surface of the film. In contrast, the surface of the film before soil burial was homogeneous and continuous [Fig. 6(a)]. Observation of the fractured surface of the PVA/3 (20 wt %) blend film after soil burial for

120 days revealed that the inner part of the recovered film was not degraded by bacteria and actinomycetes, which agreed with the results of ¹H-NMR and SEC analyses.

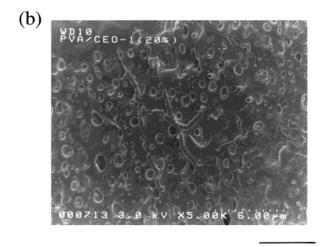
In summary, the soil burial degradation behavior of the chitin derivative-containing hybrids has been discussed by considering their thermal properties, miscibilities, surface hydrophilicities, and tacticity of PVA. It seems clear that the thermal property and miscibility of the hybrids influence the degradation acceleration of the PVA component. Thus, the PVA/**2a** (30 wt %) blend film,

Before





After



5 µm

Figure 6 SEMs of the surfaces of PVA/chitin-*graft*poly(2-ethyl-2-oxazoline) (**3**) (20 wt %): (a) before soil burial and (b) after soil burial for 120 days.

which had the lowest T_g in the PVA/2 blend films, showed the highest degradation rate in the soil. As to miscibility, there is a tendency that the lower Gordon–Taylor's k value the PVA/chitin derivative blend has, the higher the rate of weight loss in the soil. Although Gordon–Taylor's k value of the PVA/2a blend (0.21) was lower than that of PVA/2b blend (0.25), the rate of weight loss in the soil of the PVA/2a (30 wt %) blend film was higher than that of the PVA/2b (30 wt %) blend film. Similarly, the PVA/3 blend, which had a much lower k value (0.04) than the PVA/2a blend, showed a faster decrease in weight than the PVA/2a miscible blend. Therefore, molecularly miscible hybridization with biodegradable polymer, so as to enhance the decay of the bulk structure, will be an effective strategy to improve the poor biodegradability of pure PVA.

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