

Reactive Blending of Poly(L-lactic acid) with Poly(ethylene-co-vinyl alcohol)

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ABSTRACT: Poly(L-lactic acid) (PLLA) was blended with poly(ethylene-co-vinyl alcohol) (EVOH) in the presence of an esterification catalyst to induce reaction between the hydroxyl groups of EVOH and the terminal carboxylic group of PLLA. Nascent low-molecular-weight PLLA, obtained from a direct condensation polymerization of L-lactic acid in bulk state, was used for the blending. Domain size of the PLLA phase in the graft copolymer was much smaller than that corresponding to a PLLA/EVOH simple blend. The mechanical properties of the graft copolymer were far superior to those of the simple blend, and the graft copolymer exhibited excellent mechanical properties even though the biodegradable fraction substantially exceeded the percola-

tion level. The grafted PLLA reduced the crystallization rate of the EVOH moiety. Melting peak temperature (T_m) of the PLLA phase was not observed until the content of PLLA in the graft reaction medium went over 60 wt %. The modified Sturm test results demonstrated that biodegradation of EVOH-g-PLLA took place more slowly than that of an EVOH/PLLA simple blend, indicating that the chemically bound PLLA moiety was less susceptible to microbial attack than PLLA in the simple blend. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 886–890, 2005

Key words: biodegradable polymer; chain extension by grafting; poly(ethylene-co-vinyl alcohol); poly(L-lactic acid)

INTRODUCTION

Poly(L-lactic acid) has been applied to various biomedical applications, such as a controlled drug release system,^{1–4} bone fracture internal fixation,⁵ bioresorbable surgical fibers,^{6–8} and tissue engineering.⁹

Poly(L-lactic acid) is synthesized from renewable resources. As the annual crop yield of grain depends strongly on weather conditions, its price is very unstable. Hence, opening up new avenues of use for surplus grain would provide an important buffering action for price stabilization.

PLLA has a limited processing window because of the narrow gap between the melting temperature and the degradation temperature. Moreover, it is cracked easily and shows highly brittle properties.

Several approaches have been attempted to produce PLLA-based materials with a broad range of properties and improved processability, including copolymerization, stereo-complexation, and polymer blending.¹⁰

Direction condensation of L-lactic acid in the bulk state produces PLLA with low molecular weight, of the order of $\sim 10^4$ Da, due to the unfavorable reaction equilibrium constant.¹¹ The low-molecular-weight PLLA thus produced is too fragile to mold into useful articles; PLLA should have at least $\sim 10^5$ order of

molecular weight to exhibit an acceptable level of mechanical properties.

High-molecular-weight PLLA is produced commercially by ring opening polymerization of L-lactide, the latter being made by decomposition of low-molecular-weight-PLLA, which is obtained through a direct condensation polymerization of L-lactic acid. The multiple steps of the process increase considerably the production cost of PLLA. Solution polymerization of L-lactic acid also yields high-molecular-weight PLLA by using a large volume of solvent compatible with PLLA.^{12,13} In this case, a solvent with a high boiling point, such as dicyclohexylcarbodiimide or diphenyl ether, is used for the removal of by-product water by means of azeotropic distillation.¹¹ Complex facilities are needed for this process, such as purification and recycle of the used solvent. Flammability and toxicity of the solvent is another obstacle to overcome for this process to be economically competitive.

In this study, blending of low-molecular-weight PLLA, a nascent product synthesized through a direct polycondensation of L-lactic acid in bulk state, with poly(ethylene-co-vinyl alcohol) (EVOH), a synthetic polymer, was attempted to search for the possibility of production of a biodegradable material with an acceptable level of mechanical properties.

PLLA has been blended with poly(*p*-vinyl phenol),¹⁰ poly(ϵ -caprolactone),^{14,15} poly(3-hydroxyalkanoate),^{16,17} poly(ethylene oxide),^{18,19} and poly(vinyl acetate).²⁰ All the authors employed high-molecular-

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weight PLLA for the blending and, to the best of our knowledge, experimental results on blending of low-molecular-weight PLLA have never been reported in the open literature.

EVOH was selected for the host polymer, because it has hydroxyl groups to be reacted with PLLA and also has excellent processability as well as good mechanical properties. Tetrabutyl titanate was used as a catalyst to induce reaction between EVOH and PLLA.

When the biodegradable fraction in the EVOH grafted with PLLA (EVOH-g-PLLA) is higher than the percolation level (~ 30 vol %), microbes can eat holes through the polymer. Hence, the polymer does not cause the water clogging phenomenon significantly, even when discarded in soil after use so that the fertility of the soil is not adversely affected by the discarded polymer waste.

EVOH-g-PLLA synthesized in this study exhibited excellent mechanical properties up to the content of PLLA as high as 60 wt %. In sharp contrast, the EVOH/PLLA simple blend lost its mechanical properties precipitously as the content of PLLA increased.

Mechanical and thermal properties and biodegradability of the EVOH-g-PLLA are reported in this study as a function of the PLLA content. The results are compared with those of an EVOH/PLLA simple blend.

EXPERIMENTAL

Materials

1,4-Dioxane (Aldrich, Milwaukee, WI) was purified by vacuum distillation twice. L-lactic acid (LA, Aldrich, Milwaukee, WI), tetrabutoxy titanate (TNBT, Aldrich, Milwaukee, WI), and stannous octoate (Aldrich, Milwaukee, WI) were used as received. Other chemicals were used as received without further purification.

Instrumentation

Molecular weight and its distribution were measured by using GPC (Waters model 150C plus (Waters Instruments, Rochester, MN), 1,2,4-trichlorobenzene eluent, 1.0 mL/min, 135°C, column (porosity: 10 μ m, Stragel[®] HT6E (effective molecular-weight range: 5100 to 1×10^7), HT5(5100 to 4×10^6), HT3(500 to 30,000))) employing polystyrene (Showadenko SL-105, Japan) as a standard.

Thermal properties were determined by DSC (Perkin-Elmer DSC 7, Norwalk, CT). Thermal history of the products was removed by scanning from 30 to 200°C with the heating rate of 20°C/min. After cooling down the sample at 200°C/min to 30°C, it was reheated at 20°C/min to 200°C and the second scan DSC thermograms were obtained.

Blend sheets were made by hot pressing (Lab Press, CARVER) at 170°C for 1 min under 4.0 atm, and were quickly immersed into ice water. The film thus formed was free from any distortion problems.

Mechanical properties of the films were determined with a universal test machine (Instron, Model No. 4200, Canton, MA) at a cross head speed of 10mm/min according to ASTM D 638 at 20°C \pm 1°C and relative humidity of 65 \pm 2%.

SEM (S-4200, Hitachi, Japan) was used to observe the fractured surface morphology. Specimens were fractured while immersed in liquid nitrogen.

Preparation of EVOH

Poly(ethylene-co-vinyl acetate) (EVA) pellets were ground into powder (*ca.* 250 μ m). Ground EVA (6g) was saponified in 200 ml of 0.5M KOH in ethanol solution (1000 ml ethanol/28.05g KOH solution). The saponified EVA was not soluble in the reaction system. The heterogeneous solution was refluxed with stirring for 24 h, precipitated by excess distilled water, filtered, washed with distilled water and methanol, and dried in *vacuo*.

The content of the copolymers was determined from ¹H NMR peaks corresponding to methine protons (4.9 ppm) and methyl protons (2.1 ppm) of vinyl acetate units.

Polycondensation

L-lactic acid (LA) (85 wt % aqueous solution) was added to a three neck reactor (500 ml) that was connected to a vacuum system via a liquid nitrogen trap. To remove water the reactor was immersed in an oil bath at 100°C under nitrogen atmosphere for 1 h, and then stannous octoate (0.08 ml) was added to the reactor and heated at 150°C under mechanical stirring (300rpm) for 2 h. The pressure was reduced stepwise to reach 1 \sim 2 Torr, and then the reaction was continued for another 48 h. Polymers obtained were repeatedly dissolved in chloroform and precipitated from *n*-hexane to remove unreacted monomers or by-product oligomers, followed by drying at 35°C in a vacuum oven to a constant weight.

Polymer blending

The EVOH/PLLA mixture was first dissolved in 1,4-dioxane (10g in 100 ml) at 100°C and kept under an N₂ blanket. After stirring for 30 min, TNBT (0.03 ml) was added to the hot solution and stirred for 12 h. The product was precipitated in *n*-hexane and dried in *vacuo* at 60°C.

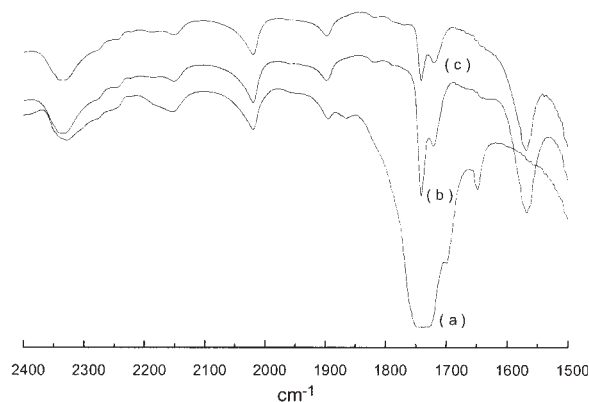


Figure 1 FTIR spectra of EVA before and after the saponification: (a) EVA, (b) after the first saponification, (c) after the fourth saponification.

Evaluation of biodegradability by the modified Sturm test

Samples to be tested were suspended in a sheet form (200 μm) in the test medium. Biodegradation was monitored at 27°C for 28 days by the modified Sturm test, using the experimental setup assembled according to ASTM D5209–91.

RESULTS AND DISCUSSION

Saponification of poly(ethylene-*co*-vinyl acetate: vinyl acetate content 10 wt %) (EVA10) was ground under cryogenic conditions to particles having *ca.* 250 μm of diameter. The EVA powder was suspended and saponified in 5M ethanol/KOH solution.

Figure 1 shows FTIR spectra of EVA and saponified EVA. Figure 1(a) corresponds to EVA before the saponification. Figure 1(b) represents EVA saponified for 12 h. The carbonyl peak appears at 1720 cm^{-1} after the first saponification, revealing that the saponification took place principally at the surface of the EVA powder because the saponification proceeded heterogeneously. The saponified powder was dissolved in toluene at 110°C and then precipitated in methanol. The precipitated product was ground and saponified

TABLE I
Characteristics of the Polymers

Sample code	T_m (°C)	T_c (°C)	ΔH_f (J/g)	M_w ($\times 10^{-3}$)
PLLA	141.8	54.6	9.3	25
EVA	89.2	77.3	35.1	291
EVOH	110.0	97.5	104.2	261

again in 5M ethanol/KOH solution for 12 h. This procedure was repeated three times, and the resulting product was subjected to FTIR measurement, which is exhibited in Figure 1(c).

It can be perceived that a small amount of vinyl acetate units of EVA still exist even after the fourth saponification (EVOH).

Table I summarizes molecular weights of EVA and EVOH measured by gel permeation chromatography (GPC). The difference between M_w of EVA and that of EVOH was larger than the theoretical difference, that is, 14,000, assuming that all the acetate groups of EVA were hydrolyzed off.

Vinyl alcohol (VOH) units are distributed randomly in EVOH, because the reactivity ratios, r_1 and r_2 , of ethylene/vinyl acetate copolymerization are both around 1.0. Hence, the segments of VOH units in sequence should be too short in length to crystallize for themselves, because the maximum content of VOH units in EVOH was as low as 3.48 mol %, assuming that all the vinyl acetate groups were hydrolyzed. Therefore, the melting behavior of EVOH should originate from melting of crystals composed of segments of ethylene units in EVOH. The higher melting peak temperature (T_m) and heat of fusion (ΔH_f) of EVOH, compared to those of EVA (Table I), are attributed to the increased intermolecular interaction due to the VOH units.

Grafting of poly(L-lactic acid) to EVOH

Poly(L-lactic acid) (PLLA) was blended with EVOH in the presence of tetrabutoxy titanate (TNBT), and some

TABLE II
Tensile Properties of PLLA/EVOH Blends

Blend composition (%)	E. modulus (MPa)	Max stress (MPa)	Elong at break (%)
PLLA	—	—	—
EVOH-g-PLLA 80	1303 \pm 493.3	0.55 \pm 0.35	1.77 \pm 0.55
EVOH-g-PLLA 60	1711 \pm 385.0	1.78 \pm 0.58	9.34 \pm 18.9
EVOH-g-PLLA 50	1661 \pm 412.9	1.59 \pm 0.72	12.2 \pm 8.12
EVOH-g-PLLA 40	1198 \pm 392.3	1.16 \pm 0.15	21.6 \pm 5.51
EVOH-g-PLLA 20	1447 \pm 355.9	1.43 \pm 0.65	9.44 \pm 2.97
EVOH	1067 \pm 453.2	1.98 \pm 0.62	16.5 \pm 4.62
EVOH/PLLA 60/40	860 \pm 643.1	1.73 \pm 0.77	2.70 \pm 1.28

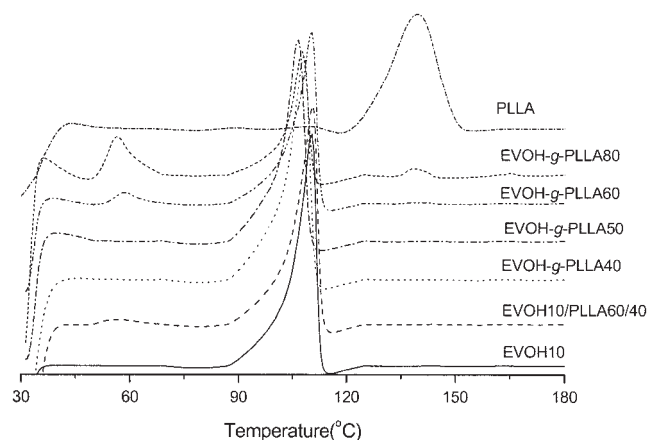


Figure 2 The second scan DSC thermograms of EVOH-g-PLLA and EVOH/PLLA blend.

of the PLLA was thought to be grafted to EVOH in dioxane at 100°C for 12 h.

Tensile properties of the resulting graft copolymer (EVOH-g-PLLA) are shown in Table II. The number after the abbreviation of EVOH-g-PLLA means the weight percentage of PLLA in the EVOH/PLLA mixture subjected to the reactive blending, and thereby, EVOH-g-PLLA 40 indicates an EVOH (6g)/PLLA (4g) mixture that was dissolved in 100 mL of 1,4-dioxane and reacted in the presence of 0.03 mL of TNBT for 12 h at 100°C under an N₂ blanket.

PLLA homopolymer, obtained from a direct condensation polymerization of L-lactic acid, had weight-average molecular weight of 2.5×10^4 . The PLLA homopolymer alone was too brittle to prepare specimens for measurement of the tensile properties.

When the low-molecular-weight PLLA was reacted with EVOH, the resulting EVOH-g-PLLA retained good tensile properties up to a content of PLLA as high as 60 wt %; and, thereafter, elongation at break of the EVOH-g-PLLA decreased sharply. It is worth noting that elongation at break of EVOH-g-PLLA contain-

TABLE III
Thermal Properties of PLLA/EVOH10 Blends

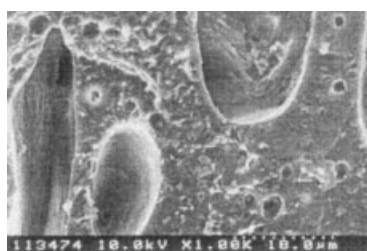
Sample code	T_m (°C)	T_c (°C)	ΔH_f (J/g)
PLLA	—	142	55
EVOH-g-PLLA 80	108	140	91
EVOH-g-PLLA 60	111	142	94
EVOH-g-PLLA 50	106	—	88
EVOH-g-PLLA 40	107	—	88
EVOH-g-PLLA 20	110	—	94
EVOH	111	—	93
EVOH/PLLA 60/40	111	142	94

ing 40 wt % of PLLA (EVOH-g-PLLA 40) was eight times higher than that of an EVOH/PLLA 60/40 simple blend.

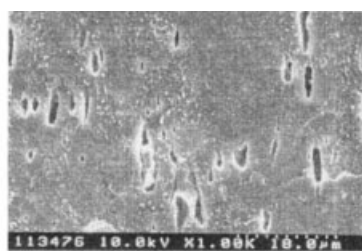
Figure 2 shows the second scan DSC thermogram of PLLA, EVOH, EVOH-g-PLLA, and EVOH/PLLA 60/40 blend. The EVOH/PLLA 60/40 blend shows two separate melting peaks located at around the melting temperatures of the corresponding parent polymers, indicating that the two polymers are phase-separated.

Thermal properties, measured by DSC of the polymers and shown in Figure 2, are collected in Table III. Crystallization peak temperature (T_c) was determined by cooling from 200°C at $-20^\circ\text{C}/\text{min}$. T_m and ΔH_f were observed while reheating the cooled sample from 30°C at $20^\circ\text{C}/\text{min}$. The EVOH/PLLA 60/40 blend had almost the same T_c at 94°C as that of EVOH. In contrast, T_c of EVOH-g-PLLA 40 appeared at 88°C, which was $6 \sim 8^\circ\text{C}$ lower than that of EVOH/PLLA 60/40. Therefore, it can be said that PLLA grafted to EVOH significantly suppressed the crystallization of the EVOH moiety.

T_m of the EVOH phase in EVOH-g-PLLA shifted to a lower temperature region as the content of PLLA increased. The T_m peak of the PLLA phase did not show up until the content of PLLA was higher than 60 wt %.



(a) EVOH/PLLA 60/40



(b) EVOH-g-PLLA 40

Figure 3 Scanning electron micrographs of the fractured surface after hydrolysis: (a) EVOH/PLLA 60/40, and (b) EVOH-g-PLLA 40.

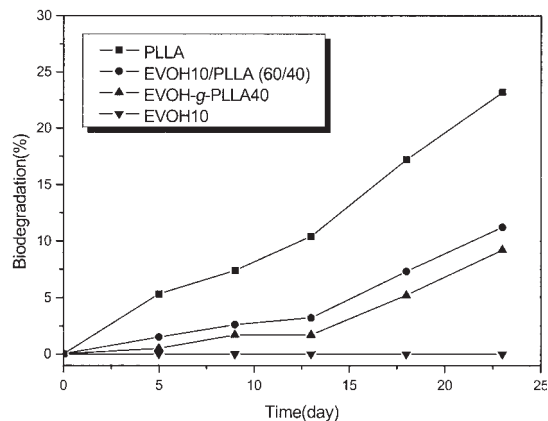


Figure 4 The modified Sturm test results of EVOH-g-PLLA 40 and EVOH/PLLA 60/40 blend.

Figure 3 shows scanning electron micrographs of fractured surfaces of EVOH/PLLA 60/40 and EVOH-g-PLLA 40. To etch the PLLA phase from the surface, the surface was subjected to hydrolysis in 1 wt % KOH solution at 30°C for 24 h.

The hydrolysis formed much larger holes in the EVOH/PLLA 60/40 blend than in EVOH-g-PLLA 40, indicating that the reaction between EVOH and PLLA, in the presence of TNBT, increased the compatibility between the two polymers. The enhanced tensile properties of EVOH-g-PLLA 40, in comparison with those of an EVOH/PLLA 60/40 simple blend, should be attributed to the improved compatibility.

Figure 4 demonstrates the modified Sturm test results of the EVOH/PLLA 60/40 blend and EVOH-g-PLLA 40. EVOH was not degraded by the microorganisms, as expected, while 25 wt % of PLLA was degraded into CO₂ over 23 days. EVOH-g-PLLA 40 showed a slightly lower biodegradability than the EVOH/PLLA 60/40 blend, revealing that ungrafted PLLA was more susceptible to microbial attack than chemically bound PLLA.

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References

- Li, G.; Cai, Q.; Bei, J.; Wang, S. *Polym Adv Technol* 2003, 14, 239.
- Liu, S. J.; Ueng, S. W.; Chan, E.-C.; Lin, S.-S.; Tsai, C.-H.; Wei, F.-C.; Shih, C.-H. *J Biomed Mater Res Part B: Appl Biomed* 1999, 48, 613.
- Furukawa, T.; Matsusue, Y.; Yasunaga, T.; Nakagawa, Y.; Okada, Y.; Shikinami, Y.; Okuno, M.; Nakamura, T. *J Biomed Mater Res* 2000, 50, 410.
- Cordewener, F. W.; Dijkgraaf, L. C.; Ong, J. L.; Agrawal, C. M.; Zardeneta, G.; Milam, S. B.; Schmitz, J. P. *J Biomed Mater Res* 2000, 50, 59.
- Rehm, K. E. *Proc 4th Int Conf on Biomaterials: Denkendorf, 1992*, 163.
- William, D. F. *Definitions in Biomaterials*; Elsevier: Amsterdam, 1997; p 49.
- Nakamura, T.; Hitomi, S.; Shimamoto, T.; Hyon, S. H.; Watanabe, S.; Shimizu, Y. *Biomaterials and Clinical Applications*; Pizzoferrato, A.; Machetti, P. G.; Ravaglioli, A.; Lee, A. J. C., Eds. Elsevier Science: Amsterdam, 1987; p 759.
- Nakamura, T.; Shimizu, Y.; Matsui, T.; Okumura, N.; Hyan, S. H.; Nishiya, K. *Proc 4th Int Conf on Biomaterials: Denkendorf, 1992*, p 153.
- Andriano, K. P.; Tabata, Y.; Ikada, Y.; Heller, J. *J Biomed Mater Res Part B: Appl Biomed* 1999, 48, 602.
- Enomoto, K.; Ajioka, M.; Yamaguchi, A. *PCT/JP 92/01638* (1993).
- Miyoshi, R.; Hashimoto, N.; Koyanagi, K.; Sumihiro, Y.; Sakai, T. *International Polymer Processing XI*, 1996, 320.
- Buchhoz, B. *Ger. Pat. 443, 542A2* (1991).
- Zhang, L.; Goh, S. H.; Lee, S. Y. *Polymer* 1998, 39, 4841.
- Hiljanen-Vainju, M.; Varpomaa, P.; Seppälä, J.; Tömälä, P. *Macromol Chem Phys* 1996, 197, 1503.
- Grijpma, D. W.; Van Hofslot, R. D.; Super, H.; Nijenhuis, A. J.; Pennings A. J. *Polym Eng Sci* 1994, 34, 1674.
- Blüm, E.; Owen, A. J. *Polymer* 1995, 36, 4077.
- Iannace, S.; Ambrosio, L.; Huang, S. J.; Nicolais, L. *J Appl Polym Sci* 1994, 54, 1525.
- Nakafuku, C. *Polym J* 1996, 28, 568.
- Nijenhuis, A. J.; Colstee, E.; Grijpma, D. W.; Pennings, A. J. *Polymer* 1996, 37, 5849.
- Gajria, A. M.; Davè, V.; Gross, R. A.; McCarthy, S. P. *Polymer* 1996, 37, 437.