Properties of a Poly(L-lactic acid)/Poly(D-lactic acid) Stereocomplex and the Stereocomplex Crosslinked with Triallyl Isocyanurate by Irradiation

Tran Minh Quynh,[1] Hiroshi Mitomo,[1] Long Zhao,[2] Masao Tamada[3]

[1]Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University, Tenjin-cho 1-5-1, Kiryu, Gunma 376-8515, Japan
[2]Advanced Materials Research Center, Nissin Electric Company, Limited, Kyoto 615-8686, Japan
[3]Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency, Watanuki-machi, Takasaki, Gunma 370-1292, Japan

ABSTRACT: A poly(L-lactic acid) (PLLA)/poly(D-lactic acid) (PDLA) stereocomplex was prepared from an equimolar mixture of commercial-grade PLLA and PDLA by melt processing for the first time. Crosslinked samples were obtained by the radiation-induced crosslinking of the poly(lactic acid) (PLA) stereocomplex mixed with triallyl isocyanurate (TAIC). The PLA stereocomplex and its crosslinked samples were characterized by their gel behavior, thermal and mechanical measurements, and enzymatic degradation. The crosslinking density of the crosslinked stereocomplex was described as the gel fraction, which increased with the TAIC content and radiation dose. The maximum crosslinking density was obtained in crosslinked samples of PLA/3% TAIC and PLA/5% TAIC irradiated at doses higher than 30 kGy. The stable crosslinking networks that formed in the irradiated PLA/TAIC substantially suppressed the segmental mobility for the crystallization of single crystals as well as stereocomplex crystals. The crosslinking network also significantly improved the mechanical properties and inhibited the enzymatic degradation of crosslinked PLA/3% TAIC. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2358–2365, 2008

Key words: mechanical properties; radiation; swelling

INTRODUCTION

Biopolymers have been intensively studied and applied in various fields as environmentally friendly materials because they are biodegradable, biocompatible, and nontoxic.[1–4] Among biopolymers, poly(lactic acid) (PLA), consisting of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA), which can be produced from renewable resources, is considered to be one of the most promising materials for replacing synthetic polymers.[5–8]

Although PLLA has a relatively high melting temperature (T_m) in comparison with other biodegradation polyesters, its T_m (ca. 180°C) is not high enough for some applications. In addition, PLLA is a semicrystalline polymer that usually crystallizes at a very low rate and produces amorphous products whose modulus drops greatly at temperatures above the glass-transition temperature (T_g). Therefore, an improvement of the heat stability of PLLA is indispensable for enhancing its applications.[3,5,9,10] Several techniques have been developed to improve the heat stability and mechanical properties of PLA-based materials.

One of the fundamental techniques used to enhance T_m of PLA is the introduction of stereocomplex crystals, which are formed in a blend of PLLA and PDLA.[11–14] Since the discovery by Ikada et al.[15] of a PLA stereocomplex between enantiomeric PLLA and PDLA with T_m about 50°C higher than that of PLLA or PDLA, great attention has been paid by scientists from different fields. The high thermal stability of the PLA stereocomplex makes it a very promising material that can be used in industry. Many researchers have reported on the preparation, crystallization, crystalline structures, and morphology of stereocomplex crystals as well as the mechanism of stereocomplex formation.[12–18] However, only a few reports on the mechanical properties of the PLA stereocomplex have been published because of the difficulties associated with the processing technique and the high cost of the PLA stereocomplex.

PLA stereocomplexes are usually prepared in solution or melt mixtures. Although the solution method is hardly to be applied in practice, melt processing of PLLA/PDLA blends requires a high processing temperature at which PLA homopolymers can be

Correspondence to: T. M. Quynh (tmqthuquynh@yahoo.com).

TABLE I
Molecular and Thermal Characteristics of Commercial-Grade PLLA and PDLA

Sample	GPC[a]		DSC				
	M_w ($\times 10^4$)	M_w/M_n	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X_c (%)[b]
PLLA	9.98	1.45	108.7	160.6	20.49	35.70	41.62
PDLA	27.98	1.42	109.1	177.1	19.87	40.59	44.79

ΔH_c = enthalpy of crystallization; ΔH_f = heat of fusion of a PLA crystal (135 J/g); ΔH_m = enthalpy of melting; GPC = gel permeation chromatography; M_n = number-average molecular weight; M_w = weight-average molecular weight; X_c = degree of crystallinity.

[a] The GPC system was equipped with a refractive-index detector (Jasco, Tokyo, Japan) with chloroform as the mobile phase and polystyrene as the standard.

[b] Calculated as $X_c = 100(\Delta H_m - \Delta H_c)/\Delta H_f$.

somewhat degraded.[19–21] Fortunately, stereocomplex structures can also form in melted mixtures of PLLA and PDLA enantiomers at temperatures lower than T_m of the stereocomplex crystals. In this case, the PLA stereocomplex can be prepared at a lower processing temperature.[13] On the other hand, the high price of the PLA stereocomplex is related to the production cost and unavailability of PDLA.[18,22] Therefore, applications of the PLA stereocomplex are still limited in biomedicine.

Recently, radiation technology has become known as a feasible tool for modifying polymer materials through degradation, crosslinking, and grafting.[23–26] Radiation crosslinking has been proved to be a potential method for improving the heat stability of PLLA. In previous studies, we have indicated that the heat stability of PLA polymers is much enhanced by radiation crosslinking in the presence of a crosslinker. Crosslinked materials of PLA polymers mixed with triallyl isocyanurate (TAIC) are characterized by very low crystallinities, and a typical crosslinking network eliminates the crystallization of crystals and reduces T_m.[27–29]

It cannot produce a complete stereocomplex because single crystals of PLLA and PDLA homopolymers predominantly form together with PLA stereocomplex crystals when the molecular weight of the homopolymer components is higher than 10^5 g/mol.[30]

In this study, we prepared a PLA stereocomplex from a melted mixture of commercial-grade PLLA and PDLA homopolymers with a 50 : 50 ratio. To improve the heat stability and mechanical properties of the PLA stereocomplex for further applications, the stereocomplexes were crosslinked with TAIC by electron-beam (EB) irradiation at different radiation doses. The crosslinking densities, described as gel fractions of the crosslinked stereocomplexes in specific solvents, and the swelling degrees of these gels in chloroform are reported. Thermal and mechanical properties of the PLA/TAIC stereocomplexes and their crosslinked samples were investigated through the TAIC content and radiation dose. The degrada-

tion of PLA stereocomplexes and their crosslinked samples were also evaluated with proteinase K for their application as environmentally friendly materials.

EXPERIMENTAL

Materials

PLLA and PDLA were purchased from Mitsui Chemical, Inc. (Tokyo, Japan), and Purac Biochem, Inc. (the Netherlands), respectively. Their molecular and thermal properties are presented in Table I. They were used for preparing the PLA stereocomplex without any further purification. TAIC was bought from Nihon Chemical Co. (Tokyo, Japan). Proteinase K (activity = 25 units/mg), hexafluoroisopropanol (HFIP), and other chemicals were purchased from Wako Chemical, Ltd. (Tokyo, Japan).

Sample preparation

Pure PLLA and PDLA with the same content were melted and then mixed together in a Labo Plastomill (Toyoseiki Co., Tokyo, Japan) at 10 cycles/min at 220°C for 10 min. After that, the blend was hot-pressed at 230°C and 100 atm for 5 min and then cold-pressed for another 5 min to obtain PLA stereocomplexes with a thickness of 0.5 mm. For preparing crosslinked samples, TAIC was added to the melted mixture of PLLA and PDLA in different weight ratios of 0.5, 1, 3, and 5%. The sample sheets were heat-sealed in a polyethylene bag *in vacuo* and EB-irradiated (EPS-750 kV, Nissinelectric, Ltd., Tokyo, Japan) at room temperature with doses ranging from 10 to 100 kGy at the same dose rate of 10 kGy/pass. The obtained samples were stored in a desiccator at room temperature before measurements.

Crosslinking behavior

Because of the low solubility of the PLA stereocomplex and its crosslinked samples in chloroform at

room temperature, their gel fractions were measured by the dissolution of the samples in a special solvent.[31] In this experiment, the gel fraction was calculated by the amount of insoluble material in HFIP with the following equation:

$$\text{Gel fraction (\%)} = (W_g/W_0) \times 100 \qquad (1)$$

where W_0 and W_g are the dried weights of the initial stereocomplex and its remaining weight (the gel component) after dissolution in HFIP at room temperature for 24 h.

The obtained gel was immersed in chloroform for 48 h, and the swelling degree (the weight ratio of the absorbed solvent to the dried gel) was calculated with the following equation:

$$\text{Degree of swelling} = [(W_s - W_g)/W_g](\rho_p/\rho_{\text{CHCl3}}) \qquad (2)$$

where W_g is the weight of the dried gel; W_s is the weight of the solvent-swollen gel of the same crosslinked sample at room temperature; and ρ_p and ρ_{CHCl3} are the densities of the polymer and chloroform, respectively. The results were reported as averages of three measurements.

Measurements

Differential scanning calorimetry (DSC) measurements were performed with a DSC-60 differential scanning calorimeter (Shimadzu, Japan) under a nitrogen atmosphere with indium as the reference sample. About 3 mg of the polymer was placed on an aluminum pan for sampling. The sample was heated from room temperature to 250°C and then cooled to 30°C at the same heating and cooling rate of 10°C/min under a nitrogen gas flow of 50 mL/min.

The mechanical properties were measured at room temperature with a Tensilon tensile tester (Toyo Baldwin, Tokyo, Japan) with a crosshead speed of 2 mm/min. Film samples were cut into rectangular strips of 40 mm × 10 mm. The film length between two gages was kept constant at 20 mm. The results are reported as averages of at least three measurements.

The dynamic mechanical analyses were carried out in air with a DMS 6100 C dynamic mechanical analyzer (Seiko Instruments, Inc., Tokyo, Japan). A sample of 20 mm × 10 mm × 0.5 mm was fixed on the sample holder. The storage modulus (E') and tan δ of each stereocomplex were recorded at a frequency of 5 Hz from room temperature to 250°C with a heating rate of 2°C/min.

Enzymatic degradations of different stereocomplexes and their crosslinked samples were estimated with proteinase K.[30,32,33] The samples were cut into

square sheets of 10 mm × 10 mm. Each sheet was separately immersed into a 10-mL buffer solution of 0.1 mol of Tris/HCl (pH 8.5) containing 1 mg of proteinase K and 1 mg of sodium azide. The polymer–enzyme solution was incubated at 37°C in a rotary shaker at 250 rpm. After each interval of 24 h, the sample sheets were taken out, washed, and dried for a day *in vacuo*. Degradation is reported as average values of weight losses (μg/mm^2) from three degraded sheets for each sample with the incubation time. For comparison, the weight losses of the same samples were measured in buffer solutions without the enzyme.

RESULTS AND DISCUSSION

Gel fraction and degree of swelling

Gel fractions and swelling degrees of crosslinked stereocomplexes are shown in Figures 1 and 2, respectively. An insignificant amount of gel was obtained in irradiated samples of PLA and PLA/0.5% TAIC stereocomplexes. At TAIC contents higher than 1%, defined gel fractions were observed in all irradiated stereocomplexes. The gel fraction increased with the radiation dose up to 30 kGy and then became saturated when the radiation dose increased again to 100 kGy. The minimum radiation dose necessary for the gel formation of crosslinked PLA/1% TAIC was higher than that of crosslinked PLLA/1% TAIC, as reported elsewhere.[26]

TAIC is a multifunctional monomer, as presented in our previous article.[27] The double bonds in TAIC molecules can easily break into monomer radicals by radiation scission, and the saturated number of monomer radicals can be attained by EB irradiation even at a low radiation dose. The number of monomer radicals produced in the PLA/TAIC stereocomplex is controlled by its weight content. However, it is more difficult to produce polymer radicals because the stereocomplex structures, including both PLLA and PDLA chains with opposite handed helices packed side by side in parallel fashion by van der Waals interactions,[16] are relatively stable. The energy required for producing a free radical of the PLA stereocomplex is higher than that of the PLA homopolymer; this is revealed as the higher minimum radiation dose necessary for gel formation of the PLA stereocomplex.

Several crosslinking points were formed in the PLA stereocomplex mixed with a low amount of TAIC by irradiation, but these crosslinking points were far from one another, so that the stable crosslinking network could not be formed in the PLA stereocomplex mixed with 0.5% TAIC, even when it was irradiated at a high radiation dose. Therefore, only insignificant amounts of organogel were
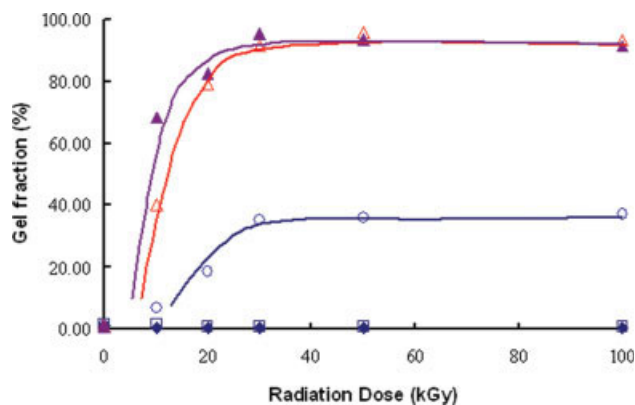
Figure 1 Gel fraction of crosslinked stereocomplexes with radiation doses: (□) the PLA stereocomplex, (◆) the PLA stereocomplex mixed with 0.5% TAIC, (○) the PLA stereocomplex mixed with 1% TAIC, (△) the PLA stereocomplex mixed with 3% TAIC, and (▲) the PLA stereocomplex mixed with 5% TAIC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observed in these samples. Moreover, the gel fraction could not be observed in PLLA mixed with a low amount of TAIC, as reported elsewhere.[26,27]

Low amounts of an irreversible gel can form in PLA and PLA/0.5% TAIC stereocomplexes. It may be formed by the crosslinking between stereocomplex microcrystals.[18,34] The gel formed by the interaction between PLLA and PDLA molecules in the PLA stereocomplex is different from the crosslinked gels between the polymer and crosslinker caused by radiation-induced crosslinking.[35] These gels are reduced with the radiation dose increasing (data are not shown) because a high radiation dose can break the interaction between enantiomeric chains.

In general, the degradation and crosslinking processes are simultaneously occurring in amorphous regions of polymers by irradiation. The presence of a crosslinker accelerates radiation crosslinking and inhibits radiation scission. Organogels could form in all the stereocomplexes crosslinked with enough TAIC, as shown in Figure 1. On the other hand, the number of polymer radicals formed in the irradiated stereocomplex increased and the average length of the polymer segment decreased with the radiation dose increasing, and this resulted in the gel fraction increasing and the swelling degree decreasing with the radiation dose. The crosslinking networks began to form in the samples crosslinked at the low radiation dose of 10 kGy, and the gel fractions increased with the radiation dose up to 30 kGy and then leveled off. Although the number of crosslinked points increased at a high radiation dose, the gel fractions seemed to become saturated. This can be explained by the stable crosslinking networks that formed in the irradiated stereocomplexes. When the radiation

dose increased again, the effects of the extensive chain scission on crystal growth produced thin crystal lamellae, and crystal defects formed. The number of imperfect crystals more or less increased with the radiation dose. The crystallization of these imperfect crystals was completely inhibited by a crosslinking network, even though they could also be immersed in the crosslinking network. The maximum gel fraction (>95%) was obtained in the PLA/3% TAIC stereocomplex irradiated at 50 kGy and in the PLA/5% TAIC stereocomplex irradiated at 30 kGy, and it was nearly saturated when the radiation dose increased again; this suggests that the radiation dose can be reduced and the content of the crosslinker can be increased to obtain the same crosslinking density.

The number of crosslinking points in the crosslinked stereocomplexes increased and a tighter crosslinking network was obtained at a higher radiation dose; therefore, the swelling capacity of the crosslinked gel with the solvent was reduced. These results are verified in Figure 2. At a higher radiation dose (>30 kGy), the swelling degrees of the stereocomplex gels crosslinked with 3 and 5% TAIC were very similar, and this suggested that a tighter crosslinking network was obtained in these samples.

Thermal analysis

The crystallization of stereocomplex crystals in PLA/TAIC stereocomplexes was confirmed by DSC as shown in Figures 3 and 4. Figure 3 shows DSC first heating curves of the PLA stereocomplex and crosslinked samples of the stereocomplex mixed with different TAIC contents and then irradiated at 50 kGy. All the stereocomplexes showed peaks around 60 and 225°C representing T_g and the melt-
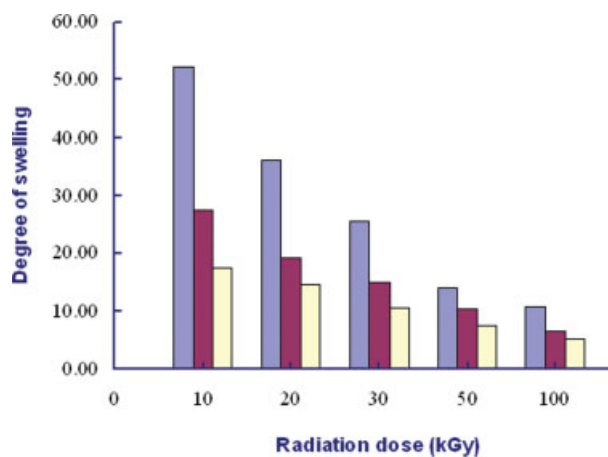
Figure 2 Degree of swelling of crosslinked samples of PLA/1% TAIC (gray bars), PLA/3% TAIC (purple bars), and PLA/5% TAIC (white bars) with the radiation dose. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
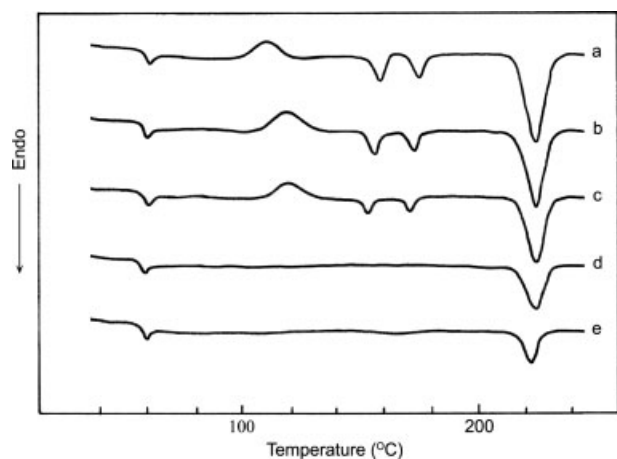
Figure 3 DSC first heating curves of (a) the PLA stereocomplex and (b) the PLA stereocomplex mixed with 0.5% TAIC, (c) the PLA stereocomplex mixed with 1% TAIC, (d) the PLA stereocomplex mixed with 3% TAIC, and (e) the PLA stereocomplex mixed with 5% TAIC and irradiated at the same radiation dose of 50 kGy.

ing temperature ($T_{m(s)}$) of the stereocomplex crystals, respectively. The DSC curve of the PLA stereocomplex reveals an exothermic peak at about 110°C and two endothermic peaks at low temperatures ranging from 155 to 175°C. These peaks are probably attributable to the cold-crystallization temperature and melting temperature ($T_{m(h)}$) of single crystals in two different phases. The stereocomplexation could not be completed because the PLA stereocomplex was obtained from high-molecular-weight PLA homopolymers in which single crystals of the homopolymers were predominantly formed.[36] As indicated by Tsuji,[17] different crystals could be formed simultaneously in the PLA stereocomplex. Stereocomplex crystals in which PLLA and PDLA chains were packed side by side or randomly were melted at a high value of $T_{m(s)}$; single crystals consisting of only pure PLA homopolymer or a mixture were melted at lower values of $T_{m(h)}$.

For PLA/TAIC stereocomplexes crosslinked at 50 kGy, the cold-crystallization peak shifted to a higher temperature, whereas the melting peaks of the homopolymers became smaller and shifted to a lower temperature. At TAIC contents higher than 3%, only $T_{m(s)}$ of the stereocomplex crystal could be observed. A high crosslinking density was obtained for the PLA/3% TAIC and PLA/5% TAIC stereocomplexes. These results confirmed that crosslinking networks were formed in the crosslinked samples of the PLA stereocomplex mixed with enough crosslinker, and the stable crosslinking network inhibited the segmental motion for crystallization. As a result, single crystals could not be crystallized in crosslinked PLA/3% TAIC and PLA/5% TAIC. More-

over, the crystallization of stereocomplex crystals was suppressed, and crystal growth was retarded.

Figure 4 shows the DSC curves of PLA/3% TAIC crosslinked at different radiation doses. The T_m values and melting enthalpies of single crystals in the crosslinked stereocomplex decreased with the radiation dose increasing to 20 kGy, and then typical crosslinked samples without melting peaks of the homopolymers were obtained in the stereocomplex crosslinked at a high dose. The crosslinking network also suppressed the segmental mobility for the crystallization of stereocomplex crystals. When the radiation dose increased, the defects of crystals may have increased, and this resulted in the formation of defective crystals or the destruction of the crystal structure. As a result, no melting peaks of the homopolymers could be observed in the stereocomplex crosslinked at doses above 30 kGy. Moreover, the stable crosslinking networks also interfered with the segmental motion for crystallization, and this evidently reduced $T_{m(s)}$ and the melting enthalpy of the stereocomplex crystals in the crosslinked PLA/3% TAIC.

Mechanical properties

The stress–strain curves of the PLA stereocomplex and crosslinked samples of PLA/TAIC irradiated at 50 kGy are plotted in Figure 5 as a function of the TAIC content. As a result of chain scission, the mechanical properties of the PLA and PLA/0.5% TAIC stereocomplexes were much reduced by irradiation. This can be explained by the fact that radiation degradation was dominant in the irradiated stereocomplex without the crosslinker. Intensive chain scission
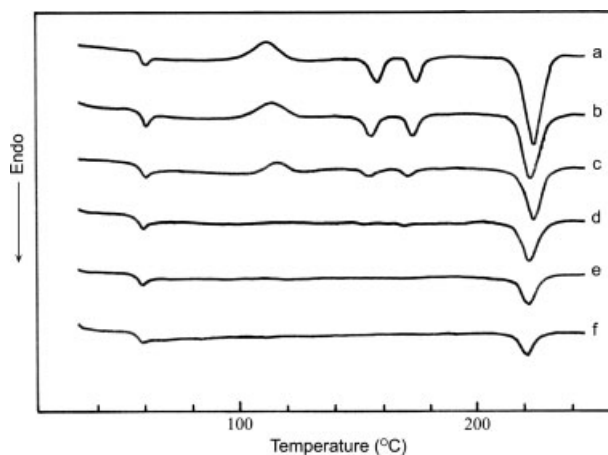
Figure 4 DSC first heating curves of (a) the PLA stereocomplex, (b) the PLA/3% TAIC stereocomplex irradiated at 10 kGy, (c) the PLA/3% TAIC stereocomplex irradiated at 20 kGy, (d) the PLA/3% TAIC stereocomplex irradiated at 30 kGy, (e) the PLA/3% TAIC stereocomplex irradiated at 50 kGy, and (f) the PLA/3% TAIC stereocomplex irradiated at 100 kGy.
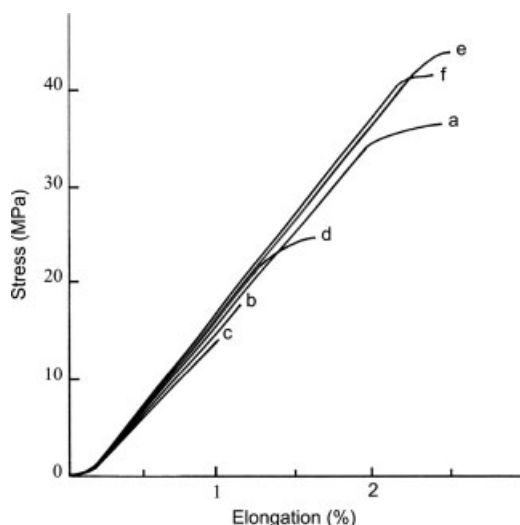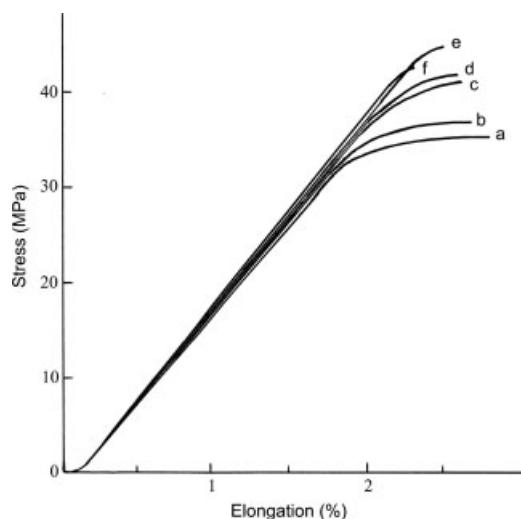
Figure 5 Stress–strain curves of (a) the PLA stereocomplex and (b) the PLA stereocomplex mixed without TAIC, (c) the PLA stereocomplex mixed with 0.5% TAIC, (d) the PLA stereocomplex mixed with 1% TAIC, (e) the PLA stereocomplex mixed with 3% TAIC, and (f) the PLA stereocomplex mixed with 5% TAIC and irradiated at the same radiation dose of 50 kGy.

reduced the length of the polymer segments, resulting in the irradiated samples becoming very weak and brittle. The mechanical properties of irradiated PLA/0.5% TAIC decreased in comparison with irradiated PLA because several crosslinking points but no stable crosslinking networks were introduced into the irradiated PLA/0.5% TAIC. Together with radiation scission, those crosslinking points made the material more heterogeneous, resulting in reductions of the tensile strength and Young's modulus. When the TAIC content increased, the mechanical properties of the crosslinked samples recovered, and even the tensile strength and Young's modulus of PLA/3% TAIC were higher than those of the initial PLA stereocomplex. This may be due to the tight crosslinking networks with high crosslinking densities produced in the PLA stereocomplexes mixed with enough TAIC, which made them become harder and tougher.

The mechanical properties of all PLA stereocomplex are listed in Table II. The tensile strength of the PLA/TAIC stereocomplexes decreased with increasing TAIC content, although the elongations at break of PLA/3% TAIC and PLA/5% TAIC were significantly improved. This may be because the effect of

TABLE II
Mechanical Properties of PLA Stereocomplexes Crosslinked with Different TAIC Contents and Different Radiation Doses

TAIC content (%)	Radiation dose (kGy)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
0	0	36.78 ± 0.24	2.23 ± 0.15	1.77 ± 0.02
	10	25.30 ± 1.91	1.62 ± 0.03	1.70 ± 0.13
	20	23.87 ± 1.27	1.48 ± 0.03	1.67 ± 0.04
	30	27.48 ± 0.91	1.28 ± 0.08	1.63 ± 0.14
	50	18.12 ± 0.43	1.13 ± 0.05	1.58 ± 0.07
	100	13.85 ± 0.10	0.95 ± 0.05	1.50 ± 0.04
0.5	0	36.70 ± 1.13	2.07 ± 0.10	1.73 ± 0.06
	10	28.08 ± 1.07	1.30 ± 0.05	1.66 ± 0.03
	20	18.59 ± 1.34	1.15 ± 0.05	1.59 ± 0.02
	30	17.40 ± 0.80	1.15 ± 0.13	1.52 ± 0.06
	50	14.61 ± 0.51	1.00 ± 0.05	1.39 ± 0.04
	100	10.03 ± 0.11	0.67 ± 0.03	1.26 ± 0.04
1	0	35.09 ± 0.51	2.35 ± 0.13	1.78 ± 0.03
	10	36.57 ± 0.35	2.30 ± 0.08	1.80 ± 0.02
	20	35.49 ± 1.78	2.20 ± 0.10	1.85 ± 0.04
	30	32.88 ± 3.14	2.07 ± 0.10	1.85 ± 0.04
	50	24.52 ± 1.73	1.62 ± 0.08	1.87 ± 0.02
	100	21.97 ± 1.75	1.47 ± 0.11	1.86 ± 0.02
3	0	34.89 ± 0.28	2.78 ± 0.08	1.78 ± 0.04
	10	35.27 ± 1.17	2.68 ± 0.13	1.84 ± 0.03
	20	41.70 ± 1.34	2.60 ± 0.08	1.86 ± 0.03
	30	**44.13** ± 1.10	**2.58** ± 0.08	**1.91** ± 0.05
	50	42.21 ± 0.20	2.48 ± 0.10	1.97 ± 0.04
	100	42.81 ± 0.73	2.30 ± 0.15	2.01 ± 0.02
5	0	33.90 ± 0.28	2.85 ± 0.10	1.82 ± 0.04
	10	37.85 ± 1.56	2.68 ± 0.18	1.86 ± 0.03
	20	38.68 ± 0.78	2.57 ± 0.10	1.90 ± 0.03
	30	**44.74** ± 3.28	**2.50** ± 0.18	**1.98** ± 0.05
	50	41.79 ± 0.75	2.38 ± 0.08	2.01 ± 0.05
	100	40.28 ± 2.33	2.23 ± 0.14	1.96 ± 0.02

Figure 6 Stress–strain curves of the PLA/3% TAIC stereocomplex irradiated at (a) 0, (b) 10, (c) 20, (d) 30, (e) 50, and (f) 100 kGy.

Figure 7 Dynamic mechanical analyses of (a) the PLA stereocomplex, (b) a crosslinked sample of PLA/3% TAIC, and (c) a crosslinked sample of PLA/5% TAIC irradiated at 50 kGy.

TAIC is similar to the influence of low-molecular-weight monomers. The stress–strain curves of the PLA/3% TAIC stereocomplex crosslinked at different doses are presented in Figure 6. Through cross-linking with 3% TAIC, the tensile strengths and Young's moduli of the crosslinked stereocomplexes increased, whereas their elongations at break slightly decreased with the radiation dose. The mechanical properties of the PLA/3% TAIC stereocomplex were significantly improved by radiation crosslinking. The crosslinking density increased, and the crosslinking network became tighter; this resulted in the higher Young's modulus.[38] The maximum tensile strength was obtained with PLA/3% TAIC crosslinked at 50 kGy, whereas its elongation at break was a little higher than that of the initial stereocomplex. These results also were verified by dynamic mechanical analyses.

Figure 7 shows E' and tan δ of the PLA stereocomplex and typical crosslinked samples as functions of temperature. The highest E' values of all the samples were about 3 GPa at room temperature, and it decreased with an increase in temperature because of thermal transitions. There were glassy, glass-transition, crystallization, rubbery, and liquid flow domains in the PLA stereocomplex [Fig. 7(a)]. Although crosslinked samples recrystallized to some extent under tensile load and at a high temperature, the crystallization domain could not be observed in the crosslinked samples [Fig. 7(b,c)]. The PLA stereocomplex was broken around 225°C (its $T_{m(s)}$), whereas the crosslinked samples were still stable over 250°C. The T_g values of the stereocomplexes are described as the peak of tan δ. Figure 7 also suggests that T_g of the crosslinked samples slightly increased
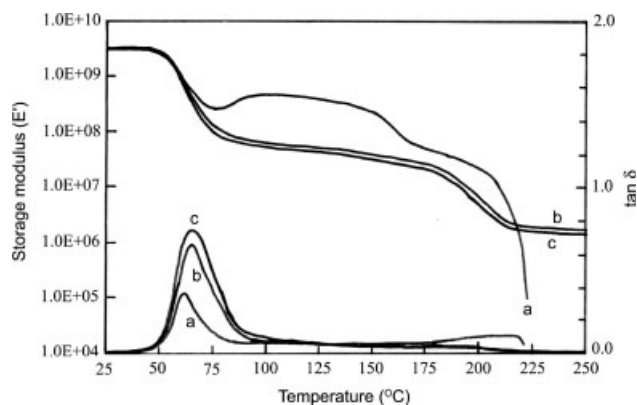
in comparison with that of the PLA stereocomplex. The E' values of PLA/3% TAIC and PLA/5% TAIC crosslinked at 50 kGy were similar, whereas their tan δ values were different. The results proved again that the mechanical properties of the PLA stereocomplex were significantly improved by radiation-induced crosslinking with TAIC.

The enzymatic degradation of each stereocomplex is described as its weight loss with the incubation time. Figure 8 shows weight losses of PLA/3% TAIC crosslinked at different radiation doses. Weight losses of all samples were linearly dependent on the degradation time. Although the PLA stereocomplex seemed not to be degraded in a buffer solution without the enzyme, the weight losses of the stereocomplex incubated with proteinase K for 1 day and
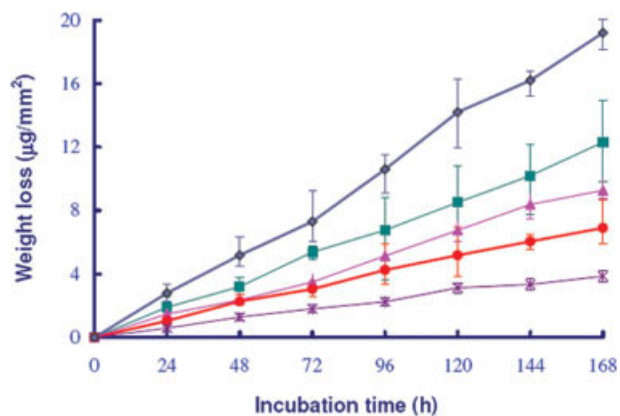
Figure 8 Enzymatic degradation of (◆) the PLA stereocomplex, (■) the PLA/3% TAIC stereocomplex crosslinked at 10 kGy, (▲) the PLA/3% TAIC stereocomplex crosslinked at 20 kGy, (●) the PLA/3% TAIC stereocomplex crosslinked at 30 kGy, and (∗) the PLA/3% TAIC stereocomplex crosslinked at 50 kGy. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

1 week were about 2.8 and 19.2 μg/mm^2, respectively. The enzymatic degradation of the PLA stereocomplex was slower than that of PLLA but much faster than that of PDLA.[28] This may have happened because proteinase K hardly cleaved the PDLA stereoisomer.[30] The crosslinking network that formed in crosslinked PLA/3% TAIC suppressed the absorption of the enzyme into the polymer, and so the cleavage process of proteinase K was inhibited. The water-solution oligomers released by enzymatic degradation may have accelerated the degradation of the PLA stereocomplexes, although the enzyme was hardly absorbed into the rigid stereocrystallites or the stable crosslinking network.

CONCLUSIONS

Different PLA stereocomplexes were prepared by the melt processing of an equimolar PLLA/PDLA mixture and crosslinked with TAIC by EB irradiation. At a low TAIC content of 0.5%, a crosslinking network was not formed in the irradiated stereocomplex, even if it was irradiated at a high radiation dose. Stable crosslinking networks were produced in the PLA stereocomplex mixed with enough TAIC (>1%) by radiation-induced crosslinking. Gel fractions of crosslinked samples increased with the TAIC content and radiation dose. The gel fractions measured with PLA/3% TAIC crosslinked at 50 kGy and PLA/5% TAIC crosslinked at 30 kGy were the same, and this suggested that similar crosslinking densities were obtained in the PLA/TAIC stereocomplex crosslinked at a lower radiation dose with increasing TAIC content. Thermal analyses revealed that the stable crosslinking network that formed in the crosslinked stereocomplex interfered with the crystallization motion of the polymer segments. Typical crosslinking networks completely suppressed the crystallization of the homopolymers and melting of single crystals and obviously lowered the melting enthalpy of the stereocomplex crystals in the PLA/3% TAIC crosslinked at doses higher than 30 kGy.

Not only the tensile strength and Young's modulus but also the elongation at break of the PLA/3% TAIC stereocomplex were significantly improved by radiation-induced crosslinking at suitable radiation doses. Dynamic mechanical analyses also revealed that the typical crosslinked stereocomplexes became stable at an elevated temperature and the crosslinking structures entirely eliminated cold crystallization. Enzymatic degradation of the crosslinked PLA stereocomplex and the crosslinked PLA/3% TAIC indicated that the weight losses of the crosslinked samples were much reduced with the radiation dose because proteinase K was hardly absorbed into the rigid stereocomplex crystallites or the stable crosslinking network.

References

1. Biodegradable Plastics and Polymers; Doi, Y.; Fukuda, K., Eds.; Studies in Polymers Science 12; Elsevier: Amsterdam, 1994.
2. Tsuji, H.; Ikada, Y. J Appl Polym Sci 1998, 67, 405.
3. Ikada, Y.; Tsuji, H. Macromol Rapid Commun 2000, 21, 117.
4. Arvanitoyannis, I. S. J Macromol Sci Rev Macromol Chem Phys 1999, 39, 205.
5. Ray, E. D.; Patrick, R. G.; David, E. H. Adv Mater 2000, 12, 2000.
6. Garlotta, D. J. Polym Environ 2001, 9, 63.
7. Leroux, J. C.; Allémann, E.; Jaeghere, F. D.; Doelker, E.; Gurny, R. J Controlled Release 1996, 39, 339.
8. Yu, L.; Dean, K.; Li, L. Prog Polym Sci 2006, 31, 576.
9. Yamane, H.; Sasai, K. Polymer 2003, 44, 2569.
10. Tsuji, H.; Fukui, I. Polymer 2003, 44, 2891.
11. Schmidt, S. C.; Hillmyer, M. A. J Polym Sci Part B: Polym Phys 2001, 39, 300.
12. Tsuji, H.; Takai, H.; Saha, S. K. Polymer 2006, 47, 3826.
13. Anderson, K. S.; Hillmyer, M. A. Polymer 2006, 47, 2030.
14. Xu, H.; Teng, C.; Yu, M. Polymer 2006, 47, 3922.
15. Ikada, Y.; Jamshidi, K.; Tsuji, H.; Hyon, S. H. Macromolecules 1987, 20, 904.
16. Brizzolara, D.; Cantow, H. J.; Diederichs, K.; Keller, E.; Domb, A. J. Macromolecules 1996, 29, 191.
17. Tsuji, H. Macromol Biosci 2005, 5, 569.
18. Fukushima, K.; Kimura, Y. Polym Int 2006, 55, 626.
19. Sodergard, A.; Stolt, M. Prog Polym Sci 2002, 27, 1123.
20. Ouchi, T.; Ichimura, S.; Ohya, Y. Polymer 2006, 47, 429.
21. Jamshidi, K.; Hyon, S. H.; Ikada, Y. Polymer 1988, 29, 2229.
22. Zhang, J. F.; Sun, X. Macromol Biosci 2004, 4, 1053.
23. Mitomo, H.; Sasada, K.; Nishimura, K.; Nagasawa, N.; Yoshii, F. J Polym Environ 2004, 12, 95.
24. Nijienhuis, A. J.; Grijpma, D. W.; Pennings, A. J. Polymer 1996, 37, 2783.
25. Burillo, G.; Clough, R. L.; Czvikovszky, T.; Guven, O.; Moel, A. L.; Liu, W.; Singh, A.; Yang, J.; Zaharescu, T. Rad Phys Chem 2002, 64, 41.
26. Jin, F.; Hyon, S. H.; Iwata, H.; Tsutsumi, S. Macromol Rapid Commun 2002, 23, 909.
27. Mitomo, H.; Kaneda, A.; Quynh, T. M.; Nagasawa, N.; Yoshii, F. Polymer 2005, 46, 4695.
28. Quynh, T. M.; Mitomo, H.; Zhao, L. Fiber Prepr 2006, 61, 109.
29. Quynh, T. M.; Mitomo, H.; Nagasawa, N.; Wada, Y.; Yoshii, F.; Tamada, M. Eur Polym J 2007, 43, 1779.
30. Reeve, M. S.; McCarthy, S. P.; Downey, M.; Gross, R. A. Macromolecules 1994, 27, 825.
31. Spinu, M.; Jackson, C.; Keating, M. Y.; Gardner, K. H. Pure Appl Chem 1996, 33, 1497.
32. Tokiwa, Y.; Jarerat, A. Biotechnol Lett 2004, 26, 771.
33. Shirahama, H.; Ichimaru, A.; Tsutsumi, C.; Nakayama, Y.; Yasuda, H. J Polym Sci Part A: Polym Chem 2005, 43, 438.
34. Lim, D. W.; Choi, S. H.; Park, T. G. Macromol Rapid Commun 2000, 21, 464.
35. Tsuji, H.; Horii, F.; Nakagawa, M.; Ikada, Y.; Odani, H.; Kitamaru, R. Macromolecules 1992, 25, 4114.
36. Tsuji, H.; Hyon, S. H.; Ikada, Y. Macromolecules 1991, 24, 5651.
37. Storey, R. F.; Wiggins, J. S.; Mauritz, K. A.; Puckett, A. D. Polym Compos 1993, 14, 17.