

Radiation-induced Crosslinking and Biodegradability of Poly(lactide) Stereocomplex

Tran Minh Quynh^{1,*}, Hiroshi Mitomo¹, Daisuke Nagai¹ and Long Zhao²

¹Department of Chemistry & Chemical Biology, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma 376-8515, Japan,

²Advanced Materials Research Center, Nissinelectric Co., Ltd. 47, Umezu-Takase-cho, Kyoto, 615-8686, Japan.

*Corresponding author. Fax: 81 277 30 1401, email: tmqthuquynh@yahoo.com.

Abstract

A novel organogel has been prepared from PLLA/PDLA stereocomplex by electron beam (EB) irradiation in the presence of triallyl isocyanurate (TAIC). The maximum crosslinking density was obtained at radiation dose of 30 kGy. The crosslinked samples revealed improved thermal and mechanical properties. Further characterization studies showed that the sample with the best thermal stability and rather good mechanical properties was obtained through irradiation followed by annealing. Biodegradability was also investigated by alkaline and enzymatic degradations. Although biodegradation of the initial PLLA/PDLA stereocomplex was delayed by crosslinking network, the crosslinked samples were significantly degraded by alkaline and proteinase K.

Key words: poly(lactic acid), stereocomplex, radiation-induced crosslinking, biodegradability

1. INTRODUCTION

Poly(lactic acid) [PLA] has been commercialized at a large scale due to its promising applicability in biomedicine, pharmacy, packaging industry as well as environmental protection [1-4]. However, the poor thermal stability [5] and mechanical properties [6] of PLA based materials have limited the utilization of them as the conventional structural materials. Recently, PLA stereocomplex between poly(L-lactic acid) [PLLA] and its enantiomer poly(D-lactic acid) [PDLA] has been intensively studied for applications required high thermal stability because its melting temperature was indicated to be 50 °C higher than that of either PLLA or PDLA [7-10].

The improved mechanical properties of 1:1 L/D stereocomplex were documented by stereocomplexation or the formation of stereo crystallites composed of L- and D-chains, resulted in three-dimensional gelation of tight packed molecular chains, suppressed the crystallization of PLA homopolymers. This microgel is unstable with hydrolysis and irradiation. On the other hand, formation of PLA stereocomplex from melt mixture of high molecular weight PLLA and PDLA can not be easily achieved and controlled. Moreover, melt processing of equimolar mixture of PLLA and PDLA required a high processing temperature, at which PLA homopolymers can be somewhat degraded.

In the previous studies, we have reported that the stable chemical gelation can be formed in PLA homopolymer as well as stereocomplex by radiation-induced crosslinking between polymer chains and crosslinker at suitable contents [11-13]. The crosslinked samples of PLA stereocomplex mixed with triallyl isocyanurate [TAIC] showed a significant improved thermal stability. In the crosslinked stereocomplex samples, the molecules of homopolymers can also crystallize separately into different homocrystallites, which influenced on their thermal properties.

Annealing treatment at the temperature higher than melting points of homopolymers ($T_{m(h)}$) can make

homocrystals in L/D stereo blend melt-crystallized into stereo crystals, whereby further improving the thermal properties of annealed samples [14]. Therefore, annealing treatment can be applied to improve thermal stability of PLA stereocomplex based materials though annealed samples usually become brittle.

In this study, the crosslinked samples were prepared from L/D stereo blends of high Mw PLLA and PDLA by electron beam irradiation and their properties were investigated with radiation doses. Since the alkaline hydrolysis as well as enzymatic degradation of L/D stereo blends were preferentially occurred at surface [15]. Controlling the surface hydrophilic of PLA materials is important for controlling their biodegradability [16]. Proteinase K and PLA degrading microorganisms hardly attacked to the crystallization and crosslinking structures existing in crosslinked PLA homopolymers [5, 11]. The crosslinking treatment can be applied to control the biodegradability of PLA stereocomplex. Therefore, the alkaline and enzymatic degradation of crosslinked L/D stereo blends were investigated. In addition, annealing treatment was also carried out at 200°C for improving thermal stability of crosslinked samples.

2. EXPERIMENTAL SECTION

2.1. Sampling

PLLA and PDLA were purchased from Toyota Motor Corporation (Japan) and Purac Biochem BV. (The Netherlands), respectively. Triallyl isocyanurate (TAIC) was supplied by Nihon Chemical Co. (Japan).

Different L/D stereo blends was obtained from melt mixture of 1:1 PLLA and PDLA with various TAIC contents in Labo Plastomill (Imoto Co., Japan) at 230°C, 10 cycle min⁻¹, for 10 min. The blends were hot-pressed at 230°C for 3 min followed by cold-pressed at room temperature for 5 min to prepare the different L/D films with thickness of 0.5 mm.

After the films were heat-sealed in polyethylene bag under vacuum then irradiated in air by electron

accelerator EPS-750kV (Nissin Electric Ltd., Japan) at the same dose rate of 10 kGy pass⁻¹ with various doses. The obtained crosslinked stereocomplex (XL/D) samples were kept in desiccator for a week to decay radicals completely and dried in vacuum before measurements. The best crosslinked sample was annealed at 200°C for 5 min to recrystallize homo crystals to stereo crystals.

2.2. Crosslinking behavior

Gel fraction of all samples was measured by dissolving the crosslinked samples in hexafluoroisopropanol (HFIP) using the following equation:

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

where W_0 is dried initial weight and W_g is dried weight of the remaining insoluble materials of crosslinked sample after it was dissolved in solvent for 24 hours.

2.3. Analysis

A sample of 5 × 4 mm in size was placed on the sample holder under the constant load of 5.0 g (about 24.5 kPa), then heated from room temperature to 275°C with heating rate of 10°C min⁻¹ under nitrogen atmosphere. The TMA elongation was recorded against temperature by thermo-mechanical analyzer (Shimadzu TMA-50, Japan).

The mechanical properties of PLA films were measured by a tensile tester (Tensilon, Toyo Baldwin, Japan) with crosshead speed of 2 mm min⁻¹. The samples were cut into strip with 30 × 10 × 0.5 mm in size for tensile test. The initial length of sample between two gages was kept constant at 20 mm. The result obtained was average from three repeated measurements.

The dynamic thermal mechanical analysis (DTMA) was carried out in dynamic mechanical analyzer, DMS 6100 C (Seiko Instruments Inc., Japan). The samples of 20 × 10 × 0.5 mm were measured at constant frequency of 5 Hz, from 25°C to 275°C, heating rate of 2°C min⁻¹ in air. The loss (E'') and storage (E') moduli were recorded against heating temperature.

An L/D stereo blend film of 10 × 10 × 0.5 mm in size was placed in a vial containing 10 ml alkaline solution of pH 12 at 37°C for investigation of its alkaline degradation. After certain periods, the samples were taken out, washed and dried in vacuum for 24 h. Remaining weight (W_{rem}) were determined by following equation.

$$W_{rem} (\%) = 100 \times W_{rd} / W_i \quad (2)$$

where W_i and W_{rd} are the dried weight of the stereo blend film before and after degradation in alkaline.

About 70 mg of L/D film was incubated in 5 ml of 0.1 mol-Tris/HCl buffer (pH 8.6) containing 1.0 mg of proteinase K and 1.0 mg of sodium azide [17] at 37°C for estimation of enzymatic degradation. After define time incubation, the film was taken out, washed with distilled water, and then dried to a constant weight in vacuum. Biodegradation was evaluated by weight loss values (mg) per unit area (cm²) as function of time. At least three films were used for each data point.

3. RESULTS AND DISCUSSIONS

3.1. Crosslinking behavior

Fig. 1 shows the gel fraction of different L/D stereo blends crosslinked with different TAIC content as functions of radiation dose. As one can be seen, an

insignificant amount of gel fraction occurred in the L/D stereo blend. It is due to the crosslinking microgels formed by weak interactions between L and D chains [18]. These crosslinks are attributed to the stereo crystallites and they can be easily broken by irradiation. The stable gel can only be obtained in the crosslinked samples of L/D mixed with more than 1% TAIC by EB irradiation. And the gelation dose (D_{gel} is radiation dose extrapolated from dose dependent gel graph to zero gel fraction) of crosslinked L/D/TAIC samples reduced with increasing of TAIC content.

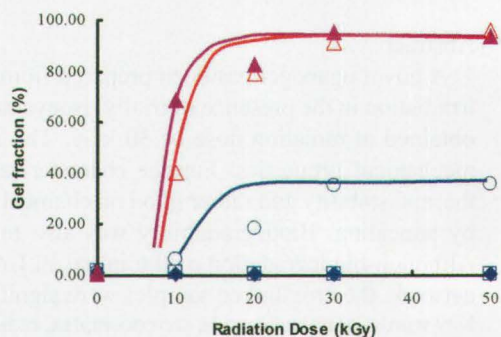


Fig.1. Gel fraction of L/D (□), L/D/0.5%TAIC (◆), L/D/1%TAIC (○), L/D/3%TAIC (△), and L/D/5%TAIC (▲) irradiated at different radiation dose.

Gel fraction, *i.e.*, the crosslinking density, increased with radiation dose and seemed to be stable over 30 kGy. The maximum gel fraction obtained with L/D/3%TAIC and L/D/5%TAIC irradiated at dose higher than 30 kGy. The high content of crosslinker is usually undesired, therefore, the L/D/3%TAIC irradiated at 30 kGy was chosen as a typical crosslinked stereo blend (XL/D) sample for next experiments. This crosslinked sample was also annealed at 200°C to estimate the effects of annealing on the properties of crosslinked stereocomplex.

3.2. Thermal stability and mechanical properties

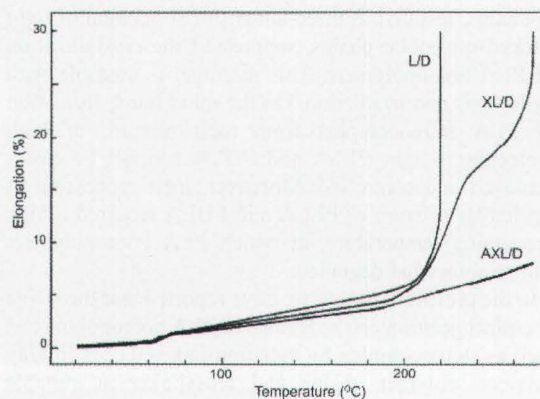


Fig.2. TMA curves of different L/D stereo blend samples.

Thermal stabilities of L/D stereo blend, its radiation crosslinking (XL/D) and annealed (AXL/D) samples were presented in Fig. 2 as function of TMA elongation with heating. Melt processing L/D stereo blend gradually elongated at about 60°C (its glass transition temperature), with the same extension rate to 200°C, then quickly

elongated and broken at around the melting temperature ($T_{m(s)}$) of stereo crystals. However, XL/D sample showed a higher thermal stability with a small elongation under 20% up to 250°C and the best thermal stability obtained with AXL/D sample that can be withstood the initial load over 270°C with the same extension.

Thus, the typical crosslinked sample of L/D stereo blend mixed with 3%TAIC became very soft and elongated to small extent as temperature rise, but it revealed the higher thermal stability over $T_{m(s)}$ of stereocomplex. Moreover, the annealed crosslinked sample showed the best thermal stability to 270°C with the smallest elongation.

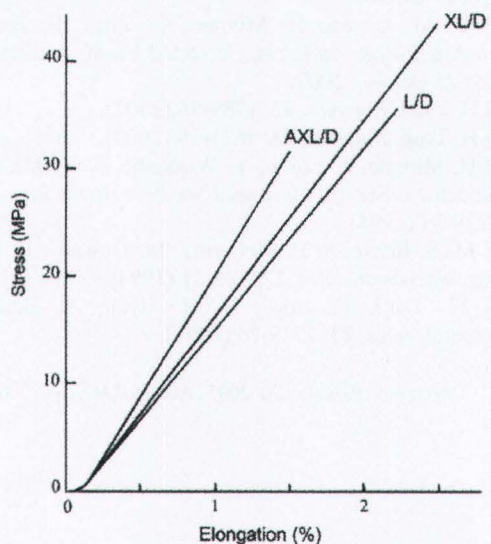


Fig.3. The stress-strain curves of different samples based on L/D stereocomplex.

Fig. 3 shows the stress-strain curves of different PLA based samples. Young's modulus of L/D stereo blend was much increased by radiation-induced crosslinking and annealing treatments. Not only stress but also elongation of crosslinked sample was significantly improved. However, annealed sample showed the lowered tensile strength and elongation. The improved mechanical properties of L/D stereo blend by radiation crosslinking can be explained by the formation of three-dimensional crosslinking network made the chain density became dense that inhibited the segmental motion for crystallization of large spherulites, resulted in the improved mechanical properties of XL/D sample. After annealing treatment, the mobility of molecular chains in the AXL/D sample much increased. In addition, the imperfect crystals that were suppressed by the crosslinking network in XL/D can re-crystallize into more perfect crystals [2]. As a result, the crystallinity of AXL/D sample significantly increased, and made it become more brittle.

The dynamic thermomechanical analyses are shown in Figure 4. Because the variation of loss modulus is similar to storage modulus, only thermograms of storage modulus (E') was presented in the present study. The E' values of all samples are stable at low temperature, and then decrease at some extents because several thermal transition as temperature rises. The E' of L/D stereo blend abruptly decreases and the sample broke at around the $T_{m(s)}$ of stereo crystals, whereas other samples can withstand over this temperature with relative high value.

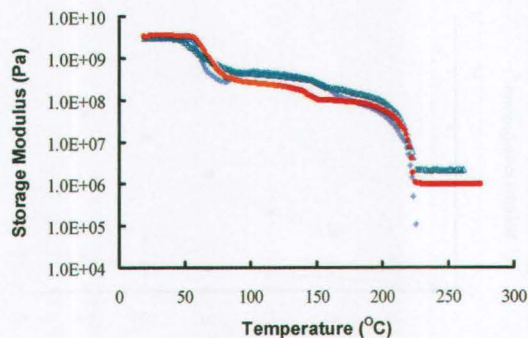


Fig.4. The storage modulus (E') of L/D stereo blend (◆), XL/D (△), and AXL/D (●) as functions of temperature.

The crosslinking network not only completely inhibited the thermal recrystallization of crystals in XL/D and AXL/D samples, but also made them become stable at high temperature. Although the E' of AXL/D was much reduced by annealing treatment, it had withstood heating to 270°C. The results suggested again that the thermal stability of annealed crosslinked sample much improved though its mechanical properties slightly reduced.

3.3. Biodegradability

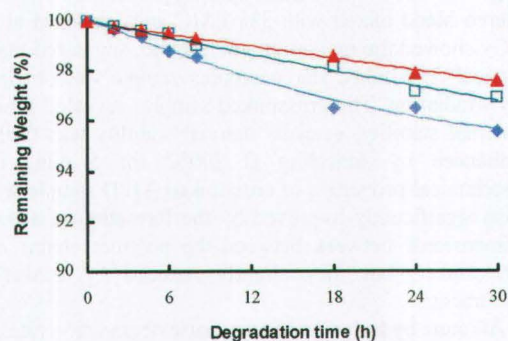


Fig.5. Remaining weight of L/D (◆), XL/D (□), and AXL/D (●) after alkaline hydrolysis.

Figure 5 shows remaining weight of L/D sample after incubation in alkaline with different intervals. All samples were significantly degraded in alkaline at pH 12. The remaining weight of XL/D higher than that of initial L/D stereo blend because the crosslinking network inhibited the absorption of alkaline into polymer matrix, and the hydrolysis primarily occurred at surface of crosslinked sample. Annealed sample showed the highest remaining weight, suggesting that the alkaline hydrolysis were hardly occurred in the crystallized structures of stereo blend. Hydrolysis has been also reported to be little effect on crystalline PLLA.

The enzymatic degradation of different L/D stereo blend samples that incubated in buffer containing proteinase K were also presented in Figure 6 as function of weight loss with degradation time. L/D stereo blend film seems not or insignificantly hydrolyzed in buffer without enzyme, whereas it was considerably degraded by proteinase K. The weight losses of L/D stereo blend were 2.8 and 19.2 $\mu\text{g}/\text{mm}^2$ after one day and one week incubated with proteinase K.

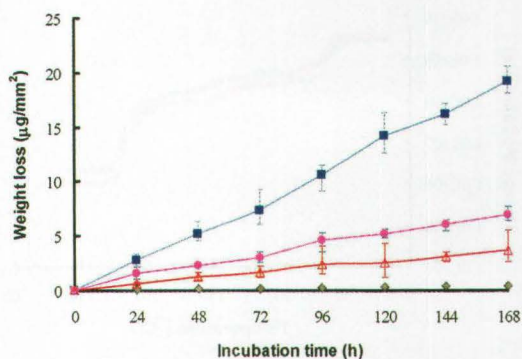


Fig. 6. Weight loss of L/D in buffer (◆), and L/D (■), XL/D (●) and AXL/D (△) incubated with proteinase K.

In spite of the reduction of degradation rates of L/D stereo blend by radiation-induced crosslinking and annealing treatments (weight loss values of AXL/D after one week is similar to the weight loss of initial L/D after one day), the XL/D and AXL/D samples can be degraded by proteinase K at some extents.

4. CONCLUSION

The L/D stereo blends were successfully prepared from high Mw PLLA and PDLA by melt processing. The L/D stereo blend mixed with 3% TAIC and irradiated at 30 kGy showed the maximum gel fraction, suggested that a typical crosslinked stereocomplex sample was obtained by irradiation. The crosslinked samples revealed a high thermal stability, even its thermal stability was further enhanced by annealing at 200°C for 5 min. The mechanical properties of crosslinked XL/D sample were also significantly improved by the formation of a three dimensional network between the polymer chains and crosslinker, but they slightly reduced by annealing treatment.

Alkaline hydrolysis and enzymatic degradation rates of L/D stereo blend samples much decreased by radiation crosslinking and annealing treatments, because alkaline was not easily to absorb into polymer gels and proteinase K would hardly attack to crosslinking or crystalline structures. The radiation-induced crosslinking and annealing treatment can be applied to control the biodegradability of PLA stereocomplex.

ACKNOWLEDGEMENTS

This work was supported by MEXT scholarship program (Ministry of Education, Culture, Sport, Science and Technology, Japan) and Nissin Electric Co., Ltd.

References

- [1] M. H. Hartmann, "Biopolymers from renewable Resources", Ed. by D. L. Kaplan, Springer-Verlag, Berlin (1998) pp. 367-411.
- [2] D. Garlotta, *J Polym Environ.*, **9**(2), 63-84 (2001).
- [3] A. Södergård, M. Stolt, *Prog Polym Sci.*, **27**, 1123-63 (2002).
- [4] R. Auras, B. Harte, S. Selke, *Macromol Biosci.*, **4**, 835-64 (2004).
- [5] H. Mitomo, A. Kaneda, T. M. Quynh, N. Nagasawa, F. Yoshii, *Polymer*, **46**, 4695-703 (2005).
- [6] J. R. Dorgan, H. Lehermeir, M. Mang, *J Polym Environ.*, **8**, 1-9 (2000).

- [7] Y. Ikada, K. Jamshidi, H. Tsuji, S. H. Hyon, *Macromolecules*, **20**, 904-06 (1987).
- [8] G. L. Loomis, J. R. Murdoch, K. H. Gardner, *Polym Prepr.*, **2**, p.55 (1990).
- [9] K. Fukushima, Y. Kimura, *Polym Int.*, **55**, 626-42 (2006).
- [10] Y. Furuhashi, Y. Kimura, H. Yamane, *J Polym Sci Part B: Polym Phys.*, **45**, 218-28 (2007).
- [11] T. M. Quynh, H. Mitomo, N. Nagasawa, Y. Wada, F. Yoshii, M. Tamada, *Eur Polym J.*, **43**(5), 1779-85 (2007).
- [12] T. M. Quynh, H. Mitomo, L. Zhao, *Fiber Preprints*, **61**, p.109 (2006).
- [13] T. M. Quynh, H. Mitomo, L. Zhao, S. Asai, *Carbohydr Polym.*, In Press, Corrected Proof, Available online 25 October 2007.
- [14] H. Tsuji, *Polymer*, **43**, 1789-96 (2002).
- [15] H. Tsuji, *Polymer*, **41**, 3621-30 (2000).
- [16] H. Mitomo, T. Enjoji, Y. Watanabe, F. Yoshii, K. Makuuchi, T. Saito, *J Macromol Sci-Pure Appl Chem A.*, **32**, 429-34 (1994).
- [17] M. S. Reeve, S. P. McCarthy, M. Downey, R. A. Gross, *Macromolecules*, **27**, 825-31 (1994).
- [18] H. Tsuji, F. Horii, S. H. Hyon, Y. Ikada, *Macromolecules*, **24**, 2719-24 (1991).

(Received December 20, 2007 ; Accepted March 6, 2008)