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Improvement of heat stability of poly(L-lactic acid) by radiation-induced crosslinking

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Abstract

Poly(L-lactic acid) (PLLA) has poor heat stability above its glass transition temperature ($T_g \sim 60$ °C). To improve its softing above T_g, PLLA was mixed with small amount of crosslinking agents and irradiated with various irradiation doses to introduce crosslinking between polymer chains. The most effective agent for radiation crosslinking was triallyl isocyanurate (TAIC). For melt-quenched PLLA, it was found that the most optimal conditions to introduce crosslinking were around 3% of TAIC and the irradiation dose of 50 kGy. The typically crosslinked PLLA showed very low crystallinity because of wide formation of molecular chain network that inhibited molecular motion for crystallization. Notable heat stability above T_g was given by annealing of PLLA samples. Enzymatic degradation of PLLA was retarded with introduction of crosslinks.

Keywords: Poly(L-lactic acid); Radiation-induced crosslinking; Thermomechanical analysis

1. Introduction

Poly(L-lactic acid) (PLLA) is a typical biodegradable plastic obtained by synthesis of lactic acid (or lactide), which produced by fermentation of corn starch [1,2]. Therefore, PLLA is a typical sustainable biodegradable thermoplastic that can be chemically synthesized from renewable resources, which is expected to be a suitable replacement of many nonbiodegradable engineering plastics in near future. PLLA is a polymer having high melting point ~175 °C, and high crystallizability [3]. It is transparent or translucent which is very suitable to bottles containing fresh drink or cosmetics, etc. However, it has some limits, e.g. poor gas barrier and brittle properties if crystallized completely, higher production cost and so on. It usually crystallized with very slow rate, so it almost remained amorphous after injection-molding. This makes a significant softening of PLLA above the glass transition temperature (T_g) [4].

There are many approaches to give heat stability of biodegradable plastics. Stereocomplex formation between PLLA and poly(D-lactic acid) (PDLA) resulted in extraordinary high T_m (~230 °C) [5–7], annealing or crystallization with some nucleating agents [8,9] and formation nanocomposite by blending with some clays [10] also promoted heat stability of PLLA samples.

To improve heat stability, there are powerful methods to introduce crosslinking between polymer molecules by chemical and irradiation treatments. There were very few studies reported chemical crosslinking of PLLA [11]. While the radiation sterilization was usually applied to PLLA, the radiation-induced crosslinking of PLLA was widely investigated. PLLA showed a high sensitivity to γ-rays and electron beams [8,11–14]. There are recent reports concerning improvement of heat stability by introducing (γ-rays and electron beams) radiation-induced crosslinks into some biodegradable polymers [15–17]. Jin et al. reported that PLLA plate (3 mm thick) mixed with 3% of triallyl isocyanurate (TAIC) and irradiated at 10 kGy or mixed with 5% of TAIC and irradiated at 5 kGy gained 100% of gel fraction [18].

In this study, treatment conditions for the most effective introduction of crosslinking were investigated in detail, the

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most optimum concentrations of crosslinking agents, irradiation doses and so on. The thermomechanical properties of the treated PLLA were also investigated to estimate thermal stability at the temperature ranges above T_g and even above melting point (T_m). PLLA was not usually degraded by enzymes but hydrolyzed in water or more preferentially in alkaline solution [19]. There are very few bacteria, which can degrade PLLA [20,21]. However, the proteinase K was used to degrade PLLA because of resemblance to protein molecules [22]. Therefore, enzymatic degradation was carried out using proteinase K in this study.

2. Experimental

2.1. Materials

Poly(L-lactic acid) (trade name: LACEA H-100J), with number-average (M_n) and weight-average molecular weights (M_w) were 9.9×10^4 and 20.8×10^4, respectively, was kindly contributed from Mitsui Chemicals, Inc. Polydipersity (M_w/M_n) was 2.10. The melting point (T_m) and glass transition temperature (T_g) of PLLA were 159.2 and 59.3 °C, respectively. The specific rotation $[\alpha]_D^{20}$ of PLLA was −148.5°. Triallyl isocyanurate (TAIC) and trimethylallyl isocyanurate (TMAIC) were purchased from Nihon Chemicals Co. and other agents were purchased from Sigma-Aldrich Co. The toxicity rank of these agents is around 4–5 (innoxious: 0, the most toxicant: 10). TAIC, TMPTA and some others have been industrially used to improve the properties of polyolefins, rubbers, etc.

2.2. Preparation of samples and irradiations

Crosslinking agents were mixed with PLLA in a Labo Plastomill (Toyoseiki Co.) at 20 rpm, 180 °C for 10 min. Then the sample was hot-pressed at 180 °C for 3 min followed by cold-press (cooled with inner tubes filled with running water) at room temperature to form the film with thickness of 0.1 mm. For comparison, PLLA without any crosslinking agent was treated with the same procedure.

The film sample was heat-sealed in polyethylene bag in vacuum then irradiated by electron beams (dose energy: 2 MeV, dose rate: 10 kGy pass^{-1}) at the room temperature with various irradiation doses.

2.3. Gel fraction measurement

Gel fraction was measured by the weight remaining after dissolved the sample in chloroform using the following equation,

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

where W_0 is weight (dry) of the crosslinked PLLA, W_g is the weight remaining (dry gel component) of the crosslinked PLLA after dissolved in chloroform at room temperature for 48 h.

Degree of swelling (volume ratio of absorbed solvent to dry gel sample) is expressed using the following equation,

$$\text{Degree of swelling } (q) = \left[\frac{(W_s - W_g)}{W_g}\right]\left(\frac{\rho_p}{\rho_{\mathrm{CHCl_3}}}\right) \qquad (2)$$

where W_g is the weight of dry gel component in the crosslinked PLLA sample, W_s is the weight of gel component swollen at room temperature for 48 h in chloroform. ρ_p and $\rho_{\mathrm{CHCl_3}}$ are densities of PLLA and chloroform, (i.e. $\rho_p/\rho_{\mathrm{CHCl_3}} = 0.838$), respectively.

2.4. Enzymatic degradation

Enzymatic degradation of the crosslinked PLLA film was carried out 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 [22]. Proteinase K (activity: 26 units mg^{-1}) was purchased from Wako Pure Chemical Industries, Ltd. About 14 mg of the film (10×10 mm^2, 0.1 mm) was immersed into the solution at 37 °C. At least three sheets of films were used for every one data point. After incubation, the film was taken out and washed with distilled water, methanol and freeze-dried to a constant weight in vacuum. Biodegradation was evaluated by measuring weight loss values (mg) per unit area (cm^2) of the film sheets. For comparison, blank test was carried out using the same buffer solution without enzyme.

2.5. Analytical measurement

A thermomechanical analyzer (Shimadzu TMA-50) was used for evaluation of heat stability. A film 5 mm×2 mm×0.1 mm (thickness) in size was fixed to the sample holder under a constant load of 0.5 g (i.e. initial stress: 24.5 kPa), then heated up to 200 °C from 25 °C with a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. The elongation of film was recorded against the temperature.

Melting point (T_m), glass transition temperature (T_g) and enthalpy of melting (ΔH_m) of each crosslinked sample (ca. 3 mg) were measured using a differential scanning calorimeter (Shimadzu DSC-50) in a nitrogen flow with a heating rate of 10 °C min^{-1}. Degree of crystallinity was calculated using the following equation:

$$\text{Degree of crystallinity (\%)} = \left[\frac{(\Delta H_m + \Delta H_c)}{\Delta H_f}\right]\times 100 \qquad (3)$$

where ΔH_m and ΔH_c are enthalpies of melting and crystallization, respectively. ΔH_f is the heat of fusion of PLLA crystal (93 J g^{-1}).

Dynamic viscoelastic properties were measured using a dynamic mechanical analyzer DMS 6100 C (Seiko