

Melting Point Depression of UV-irradiated Poly(lactic acid) Film

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Abstract: Crosslink structure can be effectively introduced into poly(lactic acid) (PLA) by UV irradiation in the presence of a small amount of benzophenone (BP). Gel fractions of crosslinked PLA samples increased with the increasing UV energy and BP concentration due to the recombination of macroradicals generated by photoscission or hydrogen abstraction. The crosslinking lowered or even depress both the melting point and cold crystallization enthalpy of the irradiated PLA samples. The improved thermal stability of the crosslinked PLA was also observed in thermogravimetric analysis.

Introduction

Biodegradable polymers such as poly(glycolic acid), poly(lactic acid), poly(ϵ -caprolactone), poly(dioxane), poly(trimethylene carbonate) have been applied to various biomedical applications including absorbable suture, skin grafts, implants and controlled drug delivery system[1]. PLA are enantiomeric polyesters consisting of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA). PLA is biodegradable, biocompatible, non-toxic and linear aliphatic polyester obtained by polymerization of lactic acid or lactide which can be produced from renewable resources such as corn or sugar cane. The PLA can be an environmentally-friendly commodity polymer due to facile hydrolytic degradability[2,3]. However, the thermal and mechanical properties of PLA were not strong enough and may eliminate its potential application. The introduction of crosslinking is effective for enhancing the heat stability or mechanical properties. The crosslinking structure of PLA can be formed by γ -irradiation and electron beam irradiation. Nevertheless, the irradiation crosslinking of PLA materials may still lack in the practical applicability considering eco-friendliness and cost of the equipment. Fortunately, UV-induced crosslinking of polymers has become increasingly popular due to continuous and environmentally-friendly process, cost and space saving, as well as cost-effectiveness.

The purpose of this study is to improve the heat stability and mechanical properties of a commercial PLA by UV irradiation in the presence of small amounts benzophenone (BP) as a photoinitiator. The gel fraction, thermal stability and mechanical properties of the crosslinked PLA were investigated.

Experimental

Materials

A commercially available PLA was supplied from NatureWorks LLC. The benzophenone was purchased by Aldrich Chemicals.

Preparation of PLA films and UV irradiation

PLA samples containing different concentration of BP (up to 9wt%) were hot-pressed at 190°C for 2min under a pressure of 10MPa. The mold was allowed to cool under pressure to ambient temperature. The thickness of the films was measured to about 200µm. A continuous UV irradiator was used to irradiate the PLA films. The irradiation was carried out on both sides of films with a continuous UV irradiator containing D-bulb of a power of 80W/cm. Fe-doped lamp was chosen to maximize photo-crosslinking effect in longer wavelength region compared with mercury lamps. UV energy was adjusted to find optimal irradiating condition for the samples at the room temperature.

Gel fraction

Gel fraction (%GF) was measured on the basis on the vacuum-dried weight using the following equation:

$$\%GF = \left(\frac{W_g}{W_0} \right) \times 100$$

where W_0 and W_g are the dry weights of the crosslinked PLA films and gels after dissolving in chloroform at room temperature for 20min.

Thermal properties

Thermal properties of PLA samples were measured with a Perkin-Elmer Diamond DSC in nitrogen atmosphere. The melting point (T_m), glass-transition temperature (T_g) and enthalpy of melting (ΔH_m) of each sample were measured over -10°C to 200°C at a heating rate of 10°C/min. The crystallinity(χ) was determined as the ratio between the experimental value of enthalpy of melting and enthalpy of melting of a 100% crystalline polymer. The thermal stability of the samples was investigated with a thermalgravimetric analyzer (TA-Q500) under nitrogen until 500°C at a heating rate of 20°C/min.

Mechanical properties

The tensile properties of the samples were measured at room temperature using a tensile tester (Instron 4467) with crosshead speed of 0.5mm/min.

Results and Discussion

The gel fraction of the crosslinked PLA samples containing 5wt% BP depending on the UV energy are shown in Figure 1. The gel fraction of crosslinked PLA increases with increasing UV energy. The gel fraction of the crosslinked PLA samples depending on the BP concentration at the same UV energy ($160\text{J}/\text{cm}^2$) are shown in Figure 2. It can be observed that the gel fraction increases with increasing BP concentration. It is assumed that high gel fraction may be resulted from larger number of radicals assisted by higher UV energy and photoinitiator concentrations.

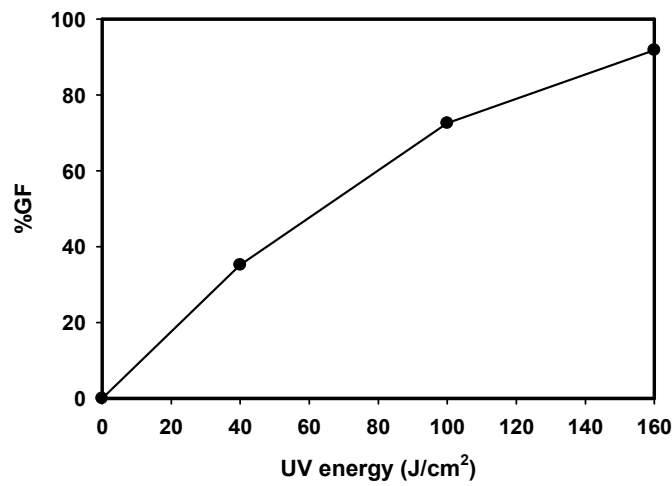


Figure 1. The gel fraction of crosslinked PLA depending on UV energy.

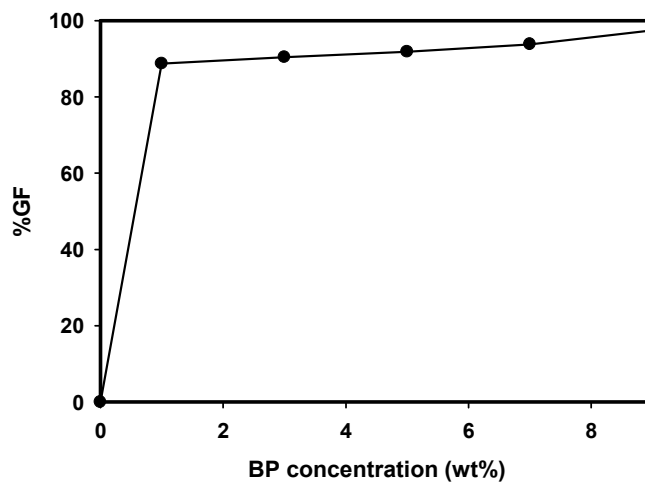


Figure 2. The gel fraction of crosslinked PLA depending on BP concentration.

The DSC results of unirradiated and crosslinked PLA samples are shown in Figure 3 and 4. Three peaks corresponding to the T_g , T_{cc} and T_m can be observed in most samples. The T_g peaks of the irradiated PLA located at the lower temperatures than that of non-crosslinked PLA, which disappeared with increasing gel fraction. Similar trend was observed for the enthalpy of cold crystallization and melting points. This may be caused by the crosslinked PLA network with a high crosslink density which inhibited segmental motion during heating. As the crosslinked structures interfered with the crystallization process, imperfect crystallites formed accordingly.

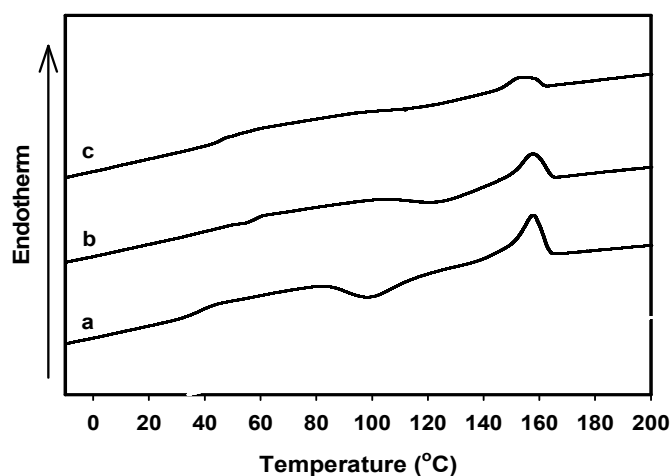


Figure 3. DSC heating curves of crosslinked PLA depending on UV energy (a) unirradiated, (b) $40\text{J}/\text{cm}^2$ and (c) $160\text{J}/\text{cm}^2$.

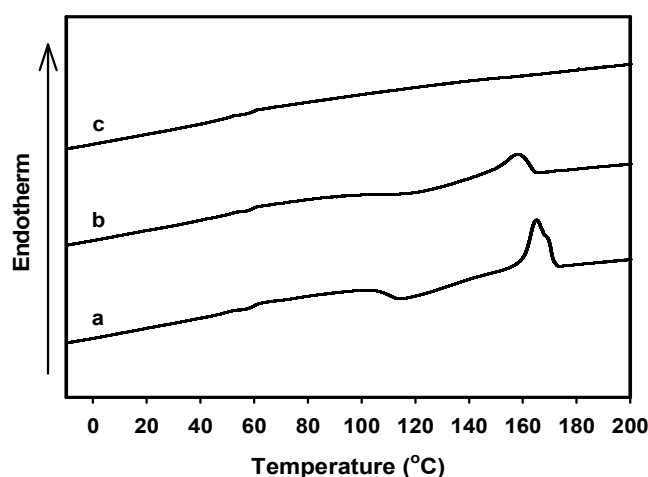


Figure 4. DSC heating curves of crosslinked PLA depending on BP concentration (a) 0wt%, (b) 1wt% and (c) 9wt%.

Conclusions

Crosslinking structure can be effectively introduced into PLA by UV irradiation in the presence of a small amount of photoinitiator (BP). Gel fraction of crosslinked PLA samples increased with the increasing UV energy and BP concentration. The crosslinking lowered or even removed both melting point and cold crystallization of irradiated PLA samples. The thermal properties of crosslinked PLA have been mainly determined by the gel fraction and crosslink density.

Acknowledgements

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