

Photocrosslinking of PLA Film Using UV Irradiation

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1. INTRODUCTION

Poly lactides (PLA) are enantiomeric polyesters including poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA). PLA is a biodegradable, biocompatible and non-toxic polyester obtained by polymerization of lactic acid or lactide which can be produced from renewable resources such as corn or sugar cane [1-2]. However, the thermal and mechanical properties of PLA were not strong enough and may eliminate its potential application. The introduction of crosslinking proved effective for enhancing the heat stability or mechanical properties of PLA materials. 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 expensive 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.

2. EXPERIMENTAL

2.1 Materials

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

2.2 Preparation of samples and irradiation

PLA samples containing different concentration of BP (up to 9wt%) were mixed and hot-pressed at 190°C for 2min to form a film in thickness of about 200 μ m. A continuous UV irradiator (Litzen, Korea) was used to irradiate the PLA films. UV energy was adjusted to find optimal irradiating condition for the samples at the room temperature.

2.3 Gel fraction

Gel fraction was measured on the basis on the vacuum-dried weight using the following equation:

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

where W_0 is the dry weight of the crosslinked PLA,

W_g is the dry weight of the crosslinked PLA after dissolving in chloroform at room temperature for 20min.

2.4 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.

3. RESULTS AND DISCUSSIONS

The gel fraction of the crosslinked PLA samples containing 5wt% BP depending on the UV energy are shown in Fig.1. It clearly shows that 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 (160J/cm²) are shown in Fig.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 concentration.

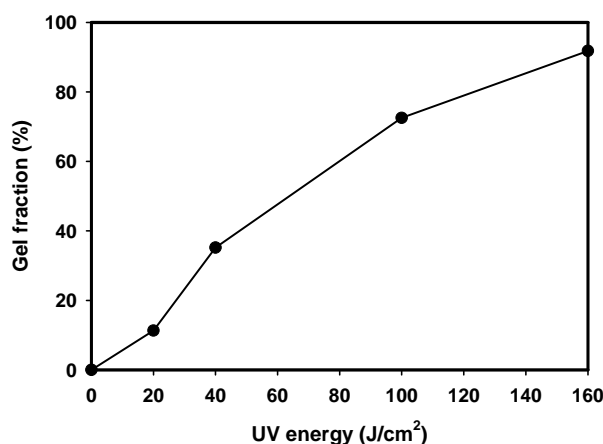


Fig. 1. The gel fraction of crosslinked PLA depending on UV energy (5wt% BP).

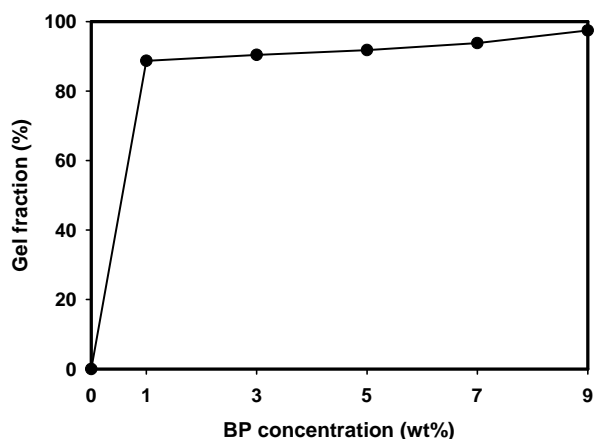


Fig. 2. The gel fraction of crosslinked PLA depending on BP concentration ($160\text{J}/\text{cm}^2$).

The DSC results of PLA and crosslinked PLA samples are shown in Fig. 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 the non-crosslinked PLA or seemed to disappear with increasing gel fraction, which was similar 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, the many imperfect crystallites were formed accordingly.

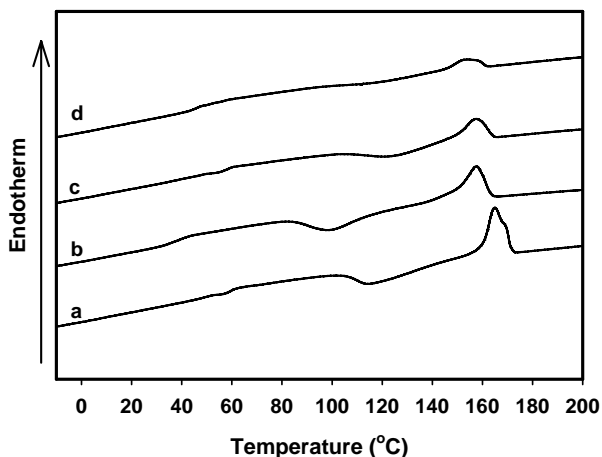


Fig. 3. DSC heating curves of PLA (a), PLA/5%BP (b) and crosslinked PLA/5%BP irradiated at $40\text{J}/\text{cm}^2$ (c), $160\text{J}/\text{cm}^2$ (d).

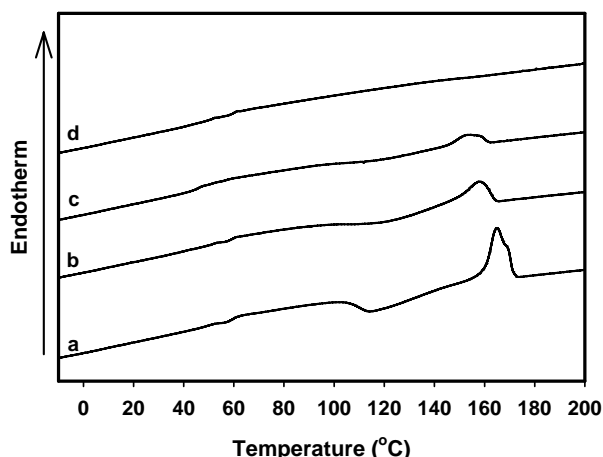


Fig. 4. DSC heating curves of PLA (a), and crosslinked PLA/1%BP irradiated at $160\text{J}/\text{cm}^2$ (b), PLA/5%BP (c), PLA/9%BP (d).

4. 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.

5. REFERENCES

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6. ACKNOWLEDGEMENTS

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