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Material Properties

Thermal and mechanical properties of chemical crosslinked polylactide (PLA)

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ABSTRACT

To improve the thermal stability and mechanical properties of PLA, crosslinking was introduced via chemical treatment of the melt by adding small amounts of crosslinking agent triallyl isocyanurate (TAIC) and dicumyl peroxide (DCP). A series of crosslinked PLA materials with different gel fraction and crosslink density were prepared. The crosslinked PLA samples were characterized by fourier transform infra-red spectrometry (FTIR). The thermal and mechanical properties of samples were also investigated by means of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile testing and dynamic mechanical analysis (DMA). The results showed that the crosslinking of PLA started at a low content of either TAIC or DCP, resulting in a decrease of crystallinity and a significant improvement of the thermal degradation initiation and completion temperatures, which indicated better thermal stability than neat PLA. Crosslinking was also responsible for the improved tensile modulus and tensile strength.

1. Introduction

Polylactide (PLA) is a typical biodegradable polyester obtained by synthesis of lactic acid (or lactide), which can be produced from renewable resources such as corn or sugarcane [1–3]. PLA is an enantiomeric polyester including poly(L-lactic acid)(PLLA) and poly(D-lactic acid)(PDLA). The chiral center in the structure allows varied enantiomeric compositions of PLA. With good biodegradability and good processability, PLA was regarded as one of the most promising biodegradable polymers and was expected to substitute some of the non-biodegradable engineering plastics [4,5]. However, the poor heat stability and mechanical properties limited its applications [6–8]. Many technologies, such as annealing, adding nucleating agents [9–12], forming composites with fiber or nanoparticles [13–16], chain extending [17,18] and introducing crosslinking structures were proved effective for enhancing the heat stability or mechanical properties of PLA materials.

The crosslinking structures of PLA can be formed by irradiation. γ-Irradiation and electron beam irradiation were widely applied to crosslinking of PLA in the presence of a small amount of crosslinking agent triallyl isocyanurate (TAIC) [19–21]. For example, Mitomo et al. reported that PLLA/(3%TAIC) irradiated at 50 kGy reached a 84% gel fraction and showed typical heat stability above the glass-transition temperature after annealing at 90 °C for 1 h [22]. Nagasawa et al. further proved that by irradiation with an electron beam, PLLA/3%TAIC showed excellent heat stability which was demonstrated by the retention of original shape at or even higher than 200 °C [23]. Nevertheless, in irradiation crosslinking of PLA materials, the radiation apparatus is expensive and the PLA products must be in the form of thin plates so as to get enough energy from the radiation to initiate the crosslinking reactions, which significantly limits the practical application of this method.

Chemical crosslinking is another possible way to introduce crosslinking structures in PLA. Some chemical reactions between the crosslinking agent and the polymer chains can be initiated by chemical treatments without irradiation, and modified PLA materials with different gel fraction and

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crosslinking density for further processing of PLA products can be obtained. For example, peroxide crosslinking of PLA with dicumyl peroxide (DCP) can form a gel structure. Nijenhuis et al. reported that at high peroxide (DCP) concentrations (13–25 wt%) and high curing temperatures (192 °C), a gel fraction of 100% could be determined gravimetrically. However, the high peroxide concentrations resulted in a steep drop of the tensile strength [24]. In addition, a large amount of chloroform solvent was required, and a further separate purification step was necessary. To the best of our knowledge, there are still very few reports on the thermal or mechanical properties of chemical crosslinked PLA materials, so further and deeper studies on the chemical crosslinking of PLA materials are to be expected.

In this article we reported our efforts on the chemical crosslinking of a commercial PLA in the presence of small amounts of TAIC and DCP, aiming at improving the thermal stability and mechanical properties. This method is economically advantageous because it was carried out in the melt state with only low amounts of TAIC and DCP, and no extra purification step and special apparatus were necessary.

2. Experimental part

2.1. Materials

A commercially available polylactide (PLA) (NatureWorks, PLA 3001D) with a melt flow index (MFI) range from 10 to 30 g/10 min (190 °C, 2.16 kg) and a density of 1.24 g/cm^3, was purchased from NatureWorks LLC. The triallyl isocyanurate (TAIC) and dicumyl peroxide (DCP) were supplied by Chen Guan Co. (Sichuan, China).

2.2. Preparation of samples

PLA samples containing different concentrations of TAIC (0.15 wt%, 0.5 wt%, 1.0 wt%, 3.0 wt%) and DCP (0.2 wt%, 0.5 wt%, 1.0 wt%, 1.5 wt%) were mixed in a Haake melt mixer at 50 rpm, 180 °C for 10 min. Then, the samples were hot-pressed at 190 °C for 3 min followed by cold-pressing at room temperature (about 20 °C) for 3 min to form the sheets with thickness of 0.8 mm. For comparison, PLA without any crosslinking agent was treated with the same procedure. The samples with 0.15 wt% TAIC and 0.5 wt% DCP (PLA-1), 0.5 wt% TAIC and 0.5 wt% DCP (PLA-2), 1.0 wt% TAIC and 1.0 wt% DCP (PLA-3), 3.0 wt% TAIC and 1.0 wt% DCP (PLA-4) were chosen for further characterization, i.e. FTIR, DSC, TGA, DMA and tensile test.

2.3. Infra-red analysis

IR spectra of pure PLA and the crosslinked PLA samples were recorded with a FTIR spectrometer (Nicolet-560, America). Before testing, the dry gel component of chemical crosslinked PLA samples was mixed with KBr powder and cold-pressed into a suitable disk for FTIR measurement.

2.4. Measurement of gel fraction and degree of swelling

Gel fraction was measured by the weight remaining after dissolving the sample in chloroform using the following Eq. (1):

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

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

Degree of swelling (volume ratio of absorbed solvent to dry gel sample) is calculated using the following Eq. (2):

$$\text{Degree of swelling } (q) = [(W_s - W_g)/W_g](\rho_P/\rho_{CHCl_3}) \tag{2}$$

where W_g is the weight of dry gel component in the crosslinked PLA sample, W_s is the weight of gel component swollen at room temperature for 48 h in chloroform ρ_P and ρ_{CHCl_3} are densities of PLA and chloroform, respectively.

2.5. Thermal analysis

The thermal properties of PLA samples (about 6 mg) were measured by DSC (Netzsch DSC-204F1) using aluminium oxide as the standard. The melting point (T_m), glass-transition temperature (T_g), enthalpy of cold crystallization (ΔH_c) and enthalpy of melting (ΔH_m) of each sample were measured from -15 °C to 200 °C under nitrogen at a heating rate of 10 °C/min.

The thermal stability of the samples (about 7 mg) was investigated with a TGA (TA-Q600) under nitrogen from room temperature (about 20 °C) to 500 °C at a heating rate of 10 °C/min.

2.6. Mechanical properties

The tensile properties of the samples were measured in accordance with ISO 527 at room temperature (about 20 °C) using a tensile tester (Instron-4302).

Dynamic mechanical properties were investigated using a dynamic mechanical analyzer DMA (TA-Q800). Samples in the form of strips (20 mm × 6 mm × 0.8 mm) were measured in tensile mode at a constant frequency of 1.0 Hz as a function of temperature from -20 °C to 200 °C at a heating rate of 3 °C/min under nitrogen flow.

2.7. Morphology observation

The fracture surfaces of pure PLA, PLA-3 and PLA-4 samples were studied with a JEOL JSM-5900LV scanning electron microscope (SEM) under an acceleration voltage of 20 kV. Prior to the SEM examination, samples were submerged in liquid nitrogen and broken to expose the internal structure for SEM studies, and all the surfaces were sputtered with gold.

3. Results and discussion

3.1. Chemical crosslinking of PLA

TAIC, whose structural formula is given in Scheme 1, has been proved to be one of the most effective crosslinking agents for PLA. The double bonds in TAIC can be easily