Materials Science Forum
ISSN: 1662-9752, Vol. 815, pp 464-469
doi:10.4028/www.scientific.net/MSF.815.464

Online: 2015-03-20

Synthesis and Characterization of Optical Active PLA Degradable Materials

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Keywords: PLA, Optical Activity, Degradability.

Abstract. An optical active Acrylate end-functionalized poly (lactic acid) (DPLA) was synthesized via melt polycondensation, with lactic acid, polyalcohol and acrylic acid as raw materials. The prepolymer products in each process were characterized by FT-IR, ^{1}H-NMR. The curing PLA coating (CPLA) was prepared using optical active DPLA, reactive diluent and photoinitiator. Gel fraction, thermal stability and degradation properties of the UV curing PLA coating properties were evaluated. The results show that branched structure of hydroxyl-terminated poly (lactic acid) (OHPLA) is beneficial to increase acrylic end capping rate (Da), Da ois as high as 88%. The structure of prepolymer and the performance of the coating are adjusted by changing content of polyalcohol. After crosslinking modification, degradation rate of CPLA is reduced and CPLA has better thermal stability than the pure PLA.

Introduction

Poly(lactic acid) (PLA) is one of the best known polymers for biodegradability[1–2]. PLA is produced from renewable biomass resources, which has renewability, biodegradability and good physical properties. PLA has now been emerging as an alternative to conventional petroleum-based polymeric materials [3].

Polymer properties can be changed and/or improved through cross-linking. Cross-linking provides polymers with properties differing from those of thermoplastic biopolymers, according to which some new synthetic routes to PLA are found[4-6]. Nowadays, bio-based thermosets have been evaluated for different applications such as coatings, inks, and adhesives [7,8]. UV-curing with the advantages of zero volatile organic compounds (VOCs), fast cure, and low energy consumption, is widely used to design biocompatible and biodegradable systems in industries of coatings and printing inks.

In this study, a UV-cured, biodegradable cross-linked poly(lactic acid) has been prepared. We chose the method of direct polycondensation which is economically advantageous to synthesis and end-functioning of PLA, instead of the ring-opening method. The objective of this work is to synthesize PLA of different cross-linked structures, and to investigate the effects of the type and content of polyhydric alcohol on the properties of thermoplastic and cross-linked PLA.

Experimental

Materials. L-lactic acid (80 %, Shenzhen Esun Industrial Co., China) was purified by rotary evaporator to reduce moisture content. Stannous chloride ($SnCl_2$), p-toluene sulfonic acid, acrylic acid (AA), pentaerythritol, toluene, hydroxyethyl methylacrylate (HEMA), diphenyl ketone, and hydroquinone were purchased from Sinopharm Shanghai Chemical Reagents Co., China.

Synthesis of hydroxyl-terminated poly(lactic acid) (OHPLA) (Step 1). Fig.1 shows the synthetic routes of PLA. The lactic acid was reacted in reaction vessel, under vigorous stirring in nitrogen atmosphere at 120 ℃ for 2 h. Then pentaerythritol with four hydroxyl groups, 0.25 wt% $SnCl_2$ and 0.25 wt% p-toluene sulfonic acid, were added to the vessel in the weight varied from 1 wt% to 35 wt%, the temperature of which was subsequently raised to 180 ℃. The product was obtained upon 8 h reaction under stirring at 180 ℃.

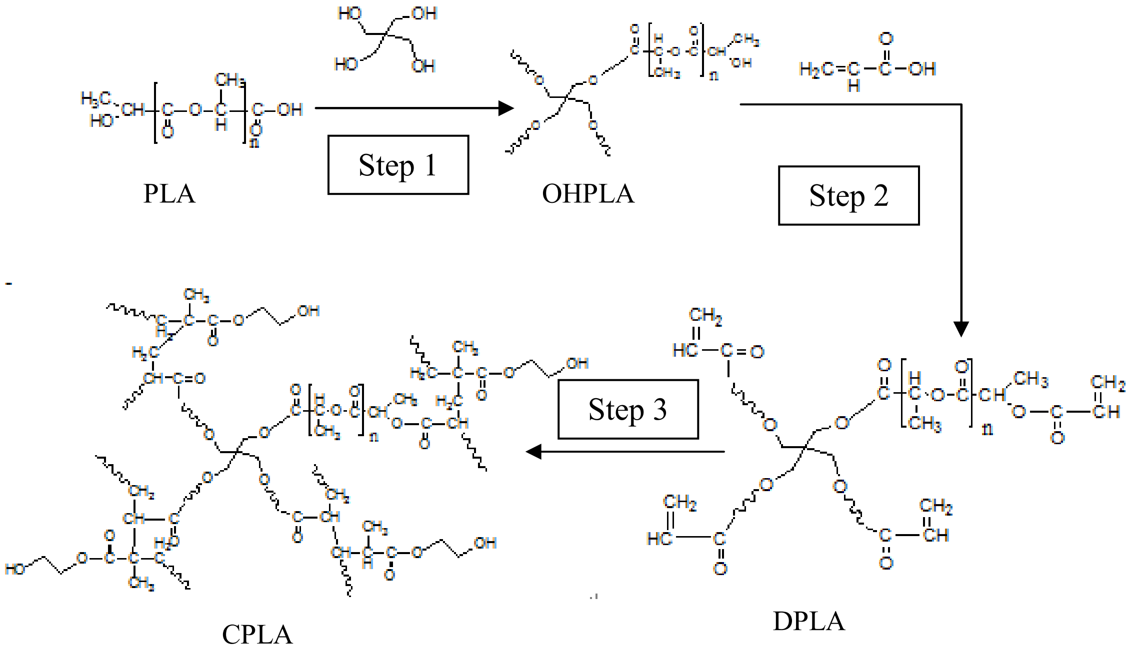

Fig.1 Schematic representation of the synthetic route of PLAs

Synthesis of acrylate-terminated poly(lactic acid) (DPLA) (Step 2). Step 2 in fig.1 shows the synthetic route of PLA that was end-functionalized with double bond from OHPLA. OHPLA and toluene in the weight ratio of 5:3 were mixed into reaction vessel. The temperature was raised to 90 °C. Then 0.15 wt% of hydroquinone and acrylic acid were gradually added into the vessel for 0.5 h. The mole number of acrylic acid was the four times of pentaerythritol mole number. Then the reaction was held at 120 °C for 4 h. Finally, the DPLA was obtained after drawing out of toluene by decompressing vacuum.

Cure of DPLA (CPLA) (Step 3). Step 3 in fig.1 shows the curing process of DPLA. DPLA, HEMA, and diphenyl ketone (DPK) were mixed uniformly at the ratio of 70:25:5 in water bath at 50 °C. The mixture was then coated on a tin plate, then it was subsequently exposed to ultraviolet (UV) light of 360 nm wavelength irradiated from a high-pressure mercury lamp for 30 min. Then the cured PLA coating (CPLA) was obtained.

PLA, OHPLA, and DPLA were all purified via re-precipitation from acetone into distilled water, followed by filtration, washing with distilled water, and drying.

Characterizations. The infrared spectrogram was obtained by Fourier transform infrared (FT-IR) spectrometer (Nicolet, 470FT-IR) with a resolution of 4 cm^{-1} and a scanning number of 32. The scanning range applied was 400–4,000 cm^{-1}.

^{1}H nuclear magnetic resonance (^{1}H-NMR) spectra were obtained using an NMR spectrometer (Varian, INOVA 600) with $CDCl_3$ as solvent.

Thermogravimetric analysis (TGA) was performed with a thermogravimetric analyzer (Beijing Optical Instruments Factory, China, TG-DTA-TG). Samples were heated from room temperature to 500 °C at a heating rate of 10 °C min−1.

Gel fraction was tested according to the following procedure. The CPLA samples were weighed after they had been dried at 60 °C for 12 h. Then they were dissolved in acetone at room temperature for 24 h. The remaining undissolved gel was dried at 60 °C for 8 h and weighed to calculate the gel fraction. Gel fraction (G) was therefore calculated using the following equation:

$$G = \frac{W_2}{W_1} \times 100\% \tag{1}$$

where W1 and W2 are the dried weights of the CPLA films and the gels after dissolution in acetone, respectively.

Thermal degradation was tested using a weight-loss method. First, a sample's original weight after thorough drying was weighed as G0; then the sample was put in a drying oven at 60℃ for a prolonged time period and weighed at preset intervals as G1. The computation formula of weight-loss rate (I1) was given as follows:

$$I_1 = \frac{G_0 - G_1}{G_0} \times 100\% \tag{2}$$

Results and Discussion

Structural characterizations of Optical Active PLA. Figs.2-5 give the FT-IR spectra and ^{1}H-NMR spectra of PLA, OHPLA and DPLA. It should be stressed that OHPLA was prepared via melt polycondensation process modification with 1 % pentaerythritol.

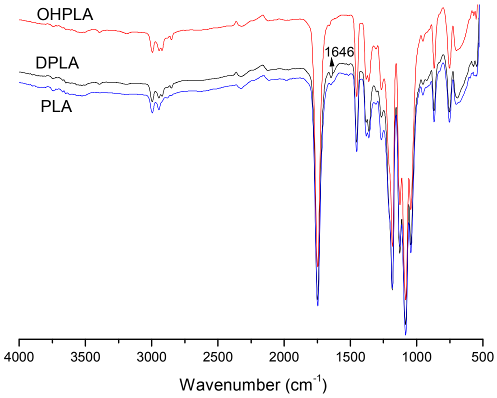

Fig.2 IR spectra of PLA, OHPLA and DPLA

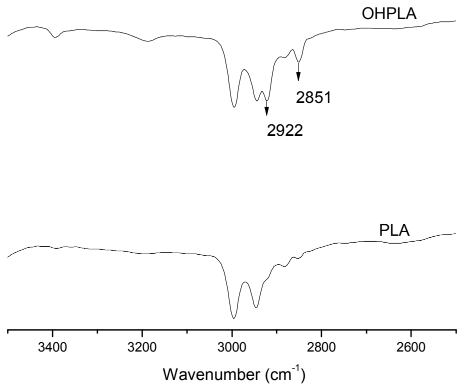

Fig.3 Partial enlarge of PLA and OHPLA in Fig.1

The FT-IR spectra Fig.2 and Fig.3 shows the characteristic peaks of 3,500 (ν O–H), 1,747 (ν C=O) and 1,300–1,000 (ν C–O) cm−1. The peak at 3,500 cm−1 of PLA and OHPLA polymers was both weak. OHPLA had new peaks at 2,922 cm−1 (antisymmetric stretching vibration) and 2,851 cm−1 (symmetric stretching vibration) for –CH2, indicating that pentaerythritol had successfully associated (esterified) with PLA. The spectra of DPLA exhibited a new peak at 1,646 cm−1 compared with that of OHPLA, which was the stretching vibration peak of –C=C. This indicates that the acrylic acid had successfully reacted with OHPLA.

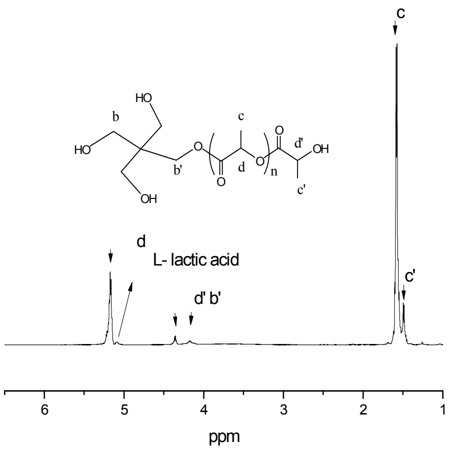

Fig.4 ^{1}H-NMR spectrum of OHPLA

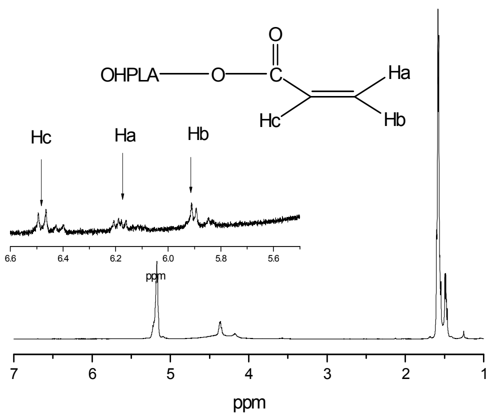

Fig.5 ^{1}H-NMR spectrum of DPLA.

^{1}H-NMR spectroscopy in Fig.4 and Fig.5 was used to characterize the microstructures of the OHPLA (modification with 1 %pentaerythritol) and DPLA, respectively. A singlet chemical shift with peak position at 1.6 ppm and a quartet with peak location at 5.2 ppm were observed in the ^{1}H-NMR spectrum of the OHPLA, which were attributed to the hydrogens (Hc and Hd), respectively, of the methyl group (–CH_3) and the methine group (–CH<) of the PLA constitutional unit respectively. The chemical shift of methine hydrogen (Hd') next to the terminal hydroxyl group was at 4.4 ppm.

The average PLA branch length of OHPLA could be estimated by comparing the peak integrations of Hd (at 5.2 ppm) and Hd' (at 4.4 ppm), which turned out to be approximately 10. The typical signal of methylene hydrogens attached to a PLA branch could be detected at 4.2 ppm. In Fig.5, the chemical shifts with peak positions at 5.9–6.5 ppm were attributed to the three hydrogens adjacent to the double bond (–CH=CH2) at chain ends.

The end capping rate (Da) of DPLA was calculated using the equation (3) according to the peak area ratio of Methylene H（b'）and macromolecular double bond H（Hb） of the ratio of peak area. Branched structure of OHPLA is beneficial to increase acrylic end capping rate(Da), Da of DPLA(1%) was as high as 88% .

$$Da = \frac{2S_{Hb}}{S_{b'}} \times 100\% \qquad (3)$$

Structure of cured PLA coating (CPLA). Fig. 6 shows the structure of CPLA. The stretching vibration peak (at ~3,500 cm^{-1}) of –OH became wider and stronger; this is due to the introduction of hydroxyl groups from the reactive diluent (HEMA). In addition, the peak at 1,646 cm^{-1} disappeared, which suggested that C=C double bonds had successfully reacted.

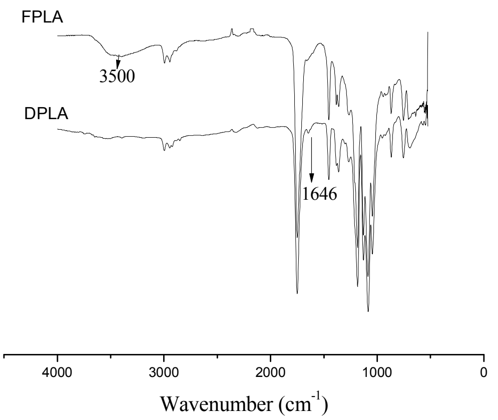

Fig. 6 The FT-IR spectra of CPLA and DPLA

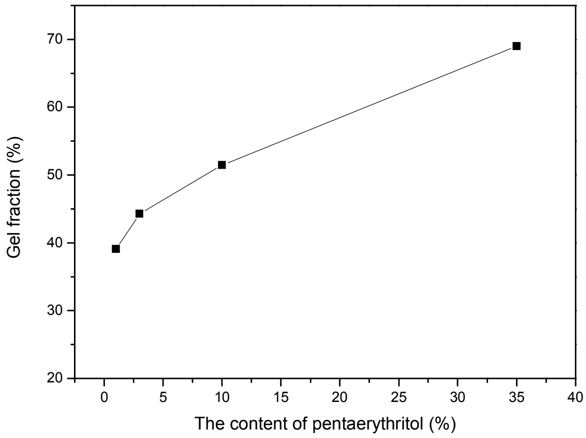

Fig.7 Gel fractions of CPLA with different pentaerythritol content

Gel Fraction of cured PLA coating (CPLA). As can be seen from the previous results, structure of DPLA was greatly affected by the degree of polycondensation reaction of lactic acid. So the photo-curing rate was not as fast as normal; the cure time was about 0.5 h. Fig.7 shows the pencil gel fraction of CPLA coating.

Fig.7 shows that the gel fraction increased with pentaerythritol content increased from 35 to 1 % in order to discuss the influence of pentaerythritol content on the structure and the gel fractions of CPLA . Under the same polymerization and photo-curing conditions, the more the content of pentaerythritol was, the shorter the average PLA branch length would be, and thus the more reactive end groups (double bonds) led to higher cross-linking density. In other words, lower pentaerythritol concentration, and thus longer PLA branch length, produced less branch-end reactive sites of the star-shaped PLA macromolecules, making it more difficult to cure via C=C double-bond addition.

Thermal degradation properties of cured PLA coating (CPLA). Thermal degradation reaction occurs when PLA is at high temperature. Thermal degradation of PLA can make end-carboxyl content increase, viscosity drop, small molecules and volatile substances generate, leading to loss of weight. The PLA thermal-degradation mechanism involves random degradation of chain ends, ester exchange, and free radical degradation[9]. PLA hydrolysis reaction causes end-carboxyl increase, and the increase of carboxyl content plays a catalytic role in the further hydrolysis of PLA; the process is a autocatalysis degradation.

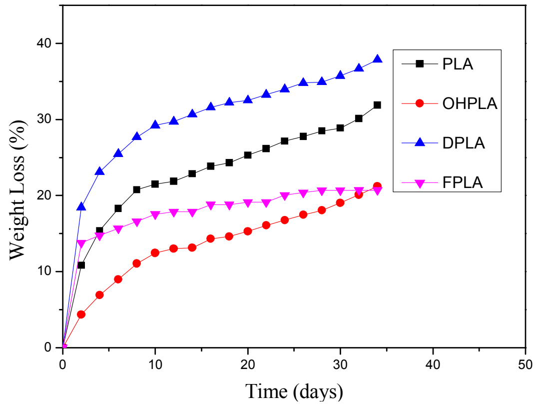

Fig.8 Thermal degradation properties of different PLAs.

Pure linear PLA and modified PLA with 1wt% pentaerythritol at different annealing stages (all crude products) were compared in thermal degradation tests (Fig.8). Linear PLA and star-shaped PLA had the same thermal degradation rule. In the first 8 days, the degradation rates were fast; and later they all became slower. The molecules of low molecular weight were easy to degrade and evaporate. After small molecules mostly evaporated, the degradation rate became slower. Generally, the degradation rates were in the order that DPLA > PLA > OHPLA. In OHPLA, inclusion of pentaerythritol reduced the number of ester groups in polymer chains compared to linear PLA, so its degradation rate was lower than linear PLA. Since the limited reaction time of OHPLA and acrylic acid (AA) made the AA conversion not high enough, there were still considerable AA monomers in DPLA, which explains for the observation that the degradation rate of DPLA was the highest. As autocatalysis degradation, it is observed from Fig.8 that the degradation began to accelerate approximately after 30 days of high-temperature annealing. Nevertheless, noticeable cross-linking CPLA effectively delayed the degradation rate.

Conclusions

PLAs were successfully synthesized via multistep reactions starting from lactic acid monomer, the microstructure and their cured coating properties were studied. The structures of PLAs at different reaction stages were determined throughout the whole process. The addition of polyhydric alcohol results in a decrease in the molecular weight of PLA, primarily due to chain scission and branching of linear PLA via alcoholysis by the polyol template. The increase content of pentaerythritol results in more reactive end groups (double bonds), and further led to higher cross-linking density. Cross-linking of PLA brought about significant increases thermal stability, as well as a decrease in thermal degradation rate.

Acknowledgments

The research was granted by the Key Project of Hubei provincial Department of Education (D20111407) and Open Fund of Hubei Provincial Key Laboratory of Green Materials for Light Industry.

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