

Kinetics of thermo-oxidative and thermal degradation of poly(D,L-lactide) (PDLLA) at processing temperature

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Abstract

Poly(D,L-lactide) (PDLLA) degraded at processing temperature under air and nitrogen. A random chain scission model was established and used to determine the activation energy E_a , and FT-IR, ^1H and ^{13}C NMR were used to elucidate the degradation behavior under different atmospheres. Results showed that there were two to three stages. The 1st stage was dominated by the oligomers containing carboxylic acid groups and hydroxyl groups, during which oxygen and nitrogen had little effect on the degradation, thus they share similar E_a . When the oligomers were consumed over or evaporated, the 2nd stage began, and oxygen had a promoting effect on the thermo-oxidation process, resulting in the great decrease in E_a . The third stage of PDLLA was observed when it degraded under nitrogen over 200 °C, which was caused by the appearance of carboxylic acid substance.

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1. Introduction

In the last decades, medical devices made up of poly(lactic acid) (PLA) have gained enormous interest in surgery applications due to its biocompatible and biodegradable nature, and due to its renewable raw material lactic acid, which is produced by microbial fermentation of biomass. The main techniques to process these materials into medical devices are compression, extrusion, injection molding and melt spinning [1]. Therefore, the oxidation and thermal degradation of them have drawn intensive attention. In order to reduce the

thermal degradation, many methods including structure designating and polymerization technology have been used. For example, in structure designing, the most widely used strategy for improving PLA processability is adding a small amount of comonomer such as D-lactide to L-lactide to obtain PDLLA [2]. The PLLA has a narrow window of processing (12 °C) whereas a 90/10 L- to D-copolymer has a much wider range of processing (40 °C) [3]. In polymerization technology, one of the effective way to achieve high molecular weight polymer is to treat polymers with chain extenders such as diisocyanates [4], considering that: (1) the high viscosity of PLA melt prevents efficient water removal in the melt condensation, (2) side-reaction leads to the formation of lactide, and (3) the high polymerization temperature required increases the thermal degradation and the racemization of polymer chains [5]. In this paper, the degradation behavior at processing temperature of PDLLA, which has been coupled with diisocyanate, was mainly investigated.

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Many researchers have done much work on the kinetics of thermal degradation of PLA, and have concluded as below. (1) Intra- and intermolecular ester exchange, which leads to the appearance of lactide and cyclic oligomers, is the dominant reaction pathway [6,7]. (2) The *cis*-elimination for polyesters, which results in small amount (<5%) of the acrylic acid and acrylic oligomers, is occurring, but is not at all a dominant reaction even at high pyrolysis temperature [8,9]. (3) Unzipping depolymer (backbiting degradation) is also observed. The lower the molecular weight, the more concentrated are the terminal hydroxyl groups, which accelerate the unzipping depolymerization and the intermolecular ester exchange. When the molecular weight of PLA is greater than 140 000 g/mol, the terminal hydroxyl concentration becomes negligible with respect to that of the ester-repeating units within the polymer chain [10].

Leiper and McNeill investigated the degradation of PLLA under both controlled heating conditions and isothermal conditions. They reported apparent activation energy E_a to be 119 kJ/mol in the range of 240–270 °C [11]. Babanalbandi et al. reported E_a values for PLLA using isothermal methods, their results showed that at first the E_a value decreased from 103 to 72 kJ/mol with increase in weight loss and then increased up to a value of 97 kJ/mol [12]. They postulated that the PLLA degradation process follows more complex kinetics, even at low conversion. Aoyagi et al. studied the degradation behavior of PLLA, and found that the E_a values changed in the range of 80–160 kJ/mol with the change in weight loss, and concluded that the pyrolysis of PLLA involved more than two mechanisms [13]. Very recently, Fan et al. reported that the E_a value was related to the residual catalyst metal, for a highly purified PLLA the E_a was 176 kJ/mol; for a PLLA with Sn content of 437 ppm the E_a value was relatively constant at 128–130 kJ/mol during the whole pyrolysis [14]. However, all the data reported were obtained from the weight loss at the pyrolysis temperature [7,11–15], which was much higher than the processing temperature. But at the processing temperature, the resins show no significant weight loss; in contrast the intrinsic viscosity of the resin changes with time. Therefore, we try to investigate the degradation behavior of PDLLA by viscosity measuring instead of the traditional methods based on the thermogravimetric analysis (TGA).

2. Experimental section

2.1. Materials and degradation of PDLLA

Poly(D,L-lactic acid) (PDLLA) was kindly supplied by Dikang Zhongke Co. Ltd (China) and was used as received. Tetrahydrofuran was used as solvent to measure its viscosity. The thermo-oxidation of PDLLA was carried out in a ventilated oven; the thermal degradation was done under nitrogen in an oil bath, with the temperature maintained at different values. Samples were taken out after a certain time interval, then intrinsic viscosity $[\eta]$ was measured using an Ubbelohde viscometer at 31 ± 0.15 °C. The molecular weight M of

PDLLA was calculated according to the Mark–Howinck equation $[\eta] = 5.50 \times 10^{-4} M^{0.639}$ [3].

2.2. Characteristics

NMR (^1H NMR: 300.1300 MHz, ^{13}C NMR: 75.4764 MHz) spectra were recorded on an AVANCE-300 NMR spectrometer (Bruker 300 MHz) in chloroform-*d* using tetramethylsilane as the internal standard. Infrared (IR) spectra were recorded on a Nicolet MX-1E FT-IR spectrometer.

2.3. Theoretical consideration

If the degradation has occurred in a random chain scission mechanism, and s bonds are broken in a single chain of X repeat unit, then we can define degree of splitting α by:

$$\alpha = s/(X_0 - 1) \quad (1)$$

where X_0 is the number-average degree of polymerization of polymer at the initial time.

If the degradation is a single molecular process, then the degradation rate ds/dt is proportion to the ester bond, that is:

$$ds/dt = k_x(X_0 - 1 - s) \quad (2)$$

where k_x is the rate constant. Integration of Eq. (2) yields:

$$s = (X_0 - 1)[1 - \exp(-k_x t)] \quad (3)$$

where k_x is the reaction rate constant. Combining Eqs. (3) and (1) yields:

$$\alpha = 1 - \exp(-k_x t) \quad (4)$$

According to the definition of the number-average degree of polymerization, we have:

$$X_t = X_0/(s + 1) \quad (5)$$

where X_t is the number-average degree of polymerization at time t . Combining Eqs (3) and (5), and eliminating s yield:

$$(X_t - 1)/X_t = [(X_0 - 1)/X_0]\exp(-k_x t) \quad (6)$$

The logarithmic function form of Eq. (6) is as following:

$$\text{Ln}[(X_t - 1)/X_t] = \text{Ln}[(X_0 - 1)/X_0] - k_x t \quad (7)$$

According to the property of logarithmic function

$$\begin{aligned} \text{Ln}(1 - 1/X_t) &= -1/X_t - (1/X_t)^{1/2}/2 - \dots - (1/X_t)^{1/n}/n - \dots \\ &\approx -1/X_t \end{aligned}$$

if $1/X_t \ll 1$. Hence when simplifying the Eq. (7), it will have the similar expression as that of Eq. (8).

$$1/X_t - 1/X_0 = -k_x t \quad (8)$$

which indicates a linear relationship between $1/X_t$ and t . Many researchers have obtained similar degradation model

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