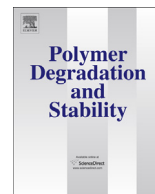




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Study on thermal degradation kinetics of cellulose-graft-poly(L-lactic acid) by thermogravimetric analysis

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ABSTRACT

The thermal degradation of cellulose-graft-poly(L-lactic acid) at different heating rates in nitrogen was studied by thermogravimetric analysis (TGA) in the temperature range 20–550 °C. Nuclear magnetic resonance (NMR), wide-angle X-ray diffraction (WAXD), and differential scanning calorimetry (DSC) analyses were utilized to determine the microstructure and glass transition temperature of cellulose-graft-poly(L-lactic acid). The kinetic parameters were determined by using Friedman, Flynn–Wall–Ozawa, and Kissinger methods. Coats–Redfern method was used to investigate the probable degradation mechanism. The results indicated that the trend of activation energy of cellulose-graft-poly(L-lactic acid) increases with increasing the content of the poly(L-lactic acid) and the process of the non-spontaneous degradation stage, goes to a random nucleation with two nuclei on the individual particle mechanism, whose rate-controlling process could be described by conversion rate (α) (integral form $1/(1 - \alpha)$).

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1. Introduction

In recent years, the development and application of biodegradable polymers, instead of the traditional use, has received a great attention due to the concerns of environmental protection and resource recycling. A major kind of biodegradable polymers is natural polymers, like cellulose. Cellulose-based materials offer excellent performances for biodegradable applications, such as biocompatibility, permeability, biological aging resistance and control-releasing potential [1–4]. Poly(L-lactic acid) (PLLA) was an authentic biopolymer as it was usually derived from agricultural products and its monomer can be produced by microbial fermentation. Due to the completely nontoxic and excellent degradability, PLLA and its polymers have been especially concerned for their applications as biomedical materials, such as degradable sutures, drug delivery systems, and temporary scaffolds for tissue [5]. Improving the thermal degradation of cellulose in these applications is a very profound subject [6,7]. A study of thermal degradation of polymers could provide practical and important

information on how polymeric materials behave under the real atmospheric conditions.

Thermogravimetric analysis (TGA) has been widely used to estimate the kinetic parameters of degradation processes, such as activation energies (E_a), reaction orders (n), and the Arrhenius pre-exponential factor (A) [8–11]. Lin et al. [8] reported the degradation kinetics of a series of polyimides and the E_a and pre-exponential factor A were determined by Coats–Redfern and Achar methods. Kinetic data obtained from TGA are very helpful to understand the thermal degradation processes and mechanisms, and also may be used as input parameters for a model of thermal degradation reaction [12]. The kinetics of cellulose pyrolysis has been reported by Sánchez-Jiménez et al. [13–15], and the model for the kinetic of the thermal degradation of cellulose has been improved.

In our previous study, cellulose-graft-poly(L-lactic acid) (CE-g-PLLA) has been successfully synthesized and the degree of polymerization of poly(L-lactic acid) (DP_{PLLA}) can be well-controlled [5,16]. The thermal degradation of CE-g-PLLA has been investigated with dynamic TGA and compared with pure cellulose (CE) and poly(L-lactic acid). It was found that the thermal degradation of CE after introducing PLLA has been improved [5]. However, the thermal degradation kinetics of CE-g-PLLA has not been studied until now, which is considered as an important property for its application [6,7]. For a further study, the kinetics of the thermal degradation of CE-g-PLLA by using different kinetic methods

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(differential and integral) under non-isothermal conditions have been thoroughly investigated, which is also the main objective of this work. The kinetic parameters, obtained from different kinetic methods, were compared and discussed.

2. Experimental

2.1. Materials

Microcrystalline cellulose (degree of polymerization of 255) was supplied by the J&K Chemical Reagent Co., Ltd, China. Poly(L-lactic acid) (M_w 50,000 g/mol) was purchased from Jinan Daigang Biomaterial Co., Ltd. CE-g-PLLA was synthesized according to our previous work [16]. All raw materials were washed with water to remove the impurity and then dried in an oven at 50 °C for 12 h.

2.2. Characterization of CE-g-PLLA

Proton nuclear magnetic resonance (^1H NMR) and Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectrum of CE-g-PLLA polymer was recorded on a Bruker AV400-MHz NMR spectrometer (Bruker, Germany). Deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$) was used as the solvent with a drop of trifluoroacetic acid-d to shift active hydrogen to lower field area, and tetramethylsilane (TMS) as an internal standard.

WAXD was performed by XRD-6000 X-ray diffractometer (Shimadzu, Japan) using Ni-filtered Cu $K\alpha$ radiation (40 kV, 30 mA) with 4°/min scanning rate at room temperature. Diffraction intensity was measured in a range of $2\theta = 5\text{--}40^\circ$.

Differential scanning calorimetry (DSC) measurement was carried out on a Q100 instruments (TA instruments, USA) equipped with a refrigerated cooling system, and an indium standard was used for calibration. Each sample was first heated from 20 to 180 °C at the rate of 10 °C/min under nitrogen to erase any previous thermal history and then was rapidly cooled to 20 °C in 6 min for subsequently carrying out the second heating scan (from 20 °C to 180 °C at the rate of 10 °C/min).

Thermogravimetric analysis (TGA) was carried on a Q50 thermogravimetric analyzer (TA instruments, USA). In this work, the mass of each sample was 3–4 mg and the carrier gas was nitrogen at a flow rate of 50 mL/min. Each sample was heated from 20 °C to 700 °C at various values of β (5, 10, 20, and 30 °C/min) to record the TGA and differential thermogravimetric analysis (DTG) curves.

2.3. Theoretical background

The degradation kinetics analyses were done using the following four methods which are summarized in Table 1. The Friedman method is a differential method, which is easy to obtain values for E_a over a wide range of conversions by plotting $\ln[\beta d\alpha/dT]$ against $1/T$ at constant value of conversion rate (α). The slope of each line is $-E_a/R$. From Flynn–Wall–Ozawa (F–W–O) method, it is easy to obtain values for E_a over a wide range of decomposition by plotting $\log\beta$ against $1/T$ at any certain conversion rate. The slope of

Table 2
Algebraic Expressions for $g(\alpha)$ for the most frequently used mechanisms of solid-state processes [24].

Symbols	$g(\alpha)$	Solid-state processes
Solid-state processes		
A_2	$[-\ln(1-\alpha)]^2$	Nucleation and growth (Avrami equation (1))
A_3	$[-\ln(1-\alpha)]^3$	Nucleation and growth (Avrami equation (2))
A_4	$[-\ln(1-\alpha)]^4$	Nucleation and growth (Avrami equation (3))
Deceleration curves		
R_1	α	Phase boundary controlled reaction (one-dimensional movement)
R_2	$2[1 - \ln(1-\alpha)^{1/2}]$	Phase boundary controlled reaction (contracting area)
R_3	$3[1 - \ln(1-\alpha)^{1/3}]$	Phase boundary controlled reaction (contracting area)
D_1	α^2	One-dimensional diffusion
D_2	$(1-\alpha)\ln(1-\alpha) + \alpha$	Two-dimensional diffusion (Valensi equation)
D_3	$[1 - \ln(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D_4	$[1 - (2/3)\alpha] - (1-\alpha)^{2/3}$	Three-dimensional diffusion (Ginstling–Brounshtein equation)
F_1	$-\ln(1-\alpha)$	Random nucleation with one nucleus on the individual particle
F_2	$1/(1-\alpha)$	Random nucleation with two nuclei on the individual particle
F_3	$1/(1-\alpha)^2$	Random nucleation with three nuclei on the individual particle

each line is $-0.4567E_a/RT$, without knowledge of the reaction order. In the Kissinger method, the plot of $\ln(\beta/T_{\max}^2)$ against $1/T_{\max}$ can be fitted to a straight line, and the E_a can be calculated from the slope of the line. T_{\max} is the peak temperature obtained from the differential thermogravimetric analysis (DTG) curve. The Coats–Redfern method uses an asymptotic approximation for the resolution at different conversion values. According to the different degradation processes, with the theoretical function $g(\alpha)$ being listed in Table 2 [24], E_a and A can be obtained from the plot of $\ln[g(\alpha)/T^2]$ against $1/T$, as well as the valid reaction mechanism.

3. Result and discussion

3.1. Nuclear magnetic resonance

A serial of CE-g-PLLA samples were synthesized by using different L-LA/MCC, as listed in Table 3. The ^1H NMR spectrum of CE-g-PLLA ($DP_{\text{PLLA}} = 3.15$) is shown in Fig. 1, where the characteristic single peaks at 1.289, 1.453, 4.209, and 5.189 ppm were attributed to terminal methyl protons A, terminal methyl protons B, terminal methine protons C, and internal methine protons D of lactyls in PLLA side-chains, respectively. The resonance peaks derived from the protons of H_1 , H_3 , H_{5+6} , H_2 , and H_4 in the anhydroglucose units appeared at 4.839, 3.859, 3.480, 3.188, and 2.985 ppm, respectively (Fig. 1). Similar phenomena were also reported by previous studies [25–27]. These results confirmed that the grafting polymerization of PLLA on the cellulose backbone was successfully processed. The average degree of polymerization

Table 1
Kinetic methods used in evaluating activation energy in this study.

Method	Expression ^a	Plots	Ref.
Friedman	$\ln(\beta d\alpha/dT) = \ln[Af(\alpha)] - E_a/RT$	$\ln(\beta d\alpha/dT)$ against $1/T$	[17,18]
Flynn–Wall–Ozawa	$\log\beta = \log[AE_a/Rg(\alpha)] - 2.315 - 0.4567E_a/RT$	$\log\beta$ against $1/T$	[19,20]
Kissinger	$\ln(\beta/T_{\max}^2) = \ln(AR/E_a) + \ln[f(\alpha)] - E_a/RT_{\max}$	$\ln(\beta/T_{\max}^2)$ against $1/T_{\max}$	[21]
Coats–Redfern	$\ln[g(\alpha)/T^2] = \ln[AR/\beta E_a] - E_a/RT$	$\ln[g(\alpha)/T^2]$ against $1/T$	[22,23]

^a β = heating rate in K min^{-1} , α = conversion rate, T = temperature in K, A = pre-exponential factor in s^{-1} , $f(\alpha)$ = the functions of conversion rate (α), E_a = activation energy in kJ mol^{-1} , R = universal gas constant (8.314 J/(mol K)).

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