Original Research

Thermal depolymerization mechanisms of poly (3-hydroxybutyrate-co-3-hydroxyvalerate)

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Abstract

Thermal degradation processes and decomposition mechanisms of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) were investigated by using thermal gravity analysis(TGA), Gel permeation chromatography (GPC), elemental analyzer, pyrolysis-gas chromatography-mass spectrometry (PyGC-MS) and ^{1}H nuclear magnetic resonance (^{1}H NMR). The degradation activation energy was calculated via the dependence of residual mass on isothermal temperature. ^{1}H NMR and PyGC-MS were used to investigate the chemical structure and component proportion of volatile gases and degradation residues which were produced by thermal decomposition, and to infer the process of macromolecular chain scission. Besides, the influence of the factors, such as outfield atmosphere, residual metal ions, on the degradation behaviors of PHBV was also studied. Finally, the PHBV thermal decomposition mechanisms were speculated on the basis of the degradation behaviors of molecular and chemical structure.

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Keywords: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV); Thermal depolymerization; Thermal degradation; Biopolymer; Polyhydroxyalkanoates(PHAs)

1. Introduction

Polyhydroxyalkanoates (PHAs), which are the only biopolyester completely synthesized through biological means, have been developed for the applications in fiber, bioplastics, implant biomaterials, drug delivery carriers, biofuels and package materials [1–3]. However, PHAs suffer from their high stereo-tacticity, low glass transition temperature, slow crystallization rate, larger spherulite size and secondary recrystallization behaviors which led to not only the fiber strand phenomena but also the existence of viscoelasticity-brittleness transition process, resulting in their brittle products and limiting its engineering application [4,5]. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is one of the typical commercialized PHAs products [6,7]. However, its high crystallinity and ordered crystal structure not only result in the brittleness but also the degradation at a temperature slightly above the melting point [8,9].

The thermal degradation behaviors of PHAs have been discussed in many literatures, in which random β-elimination is considered as the main mechanism [10,11]. In order to better understand degradation mechanisms and clarify its complex degradation behavior, the time and temperature dependent profiles of weight loss under both isothermal and non-isothermal conditions were investigated by conventional methods, such as thermal gravity analysis, differential scanning calorimetry [12], nuclear magnetic resonance [13] and mass spectrometry [14]. On the other hand, the relationship between the chemical structure of PHAs and their degradation behavior has been established by a series of multi-detection techniques in real time including thermogravimetric analyzer coupled with Fourier transform infrared spectroscopy(TG-FTIR) or mass spectrometry (TG-mass), and pyrolysis-gas chromatography mass spectrometry (PyGC-MS) [15]. Recently, Kowalczuk et al. explained the dependence of thermal stability on the chemical structure of its end groups in the form of carboxylic acid salts and proposed the corresponding E1cB mechanism [16]. Abe et al. found that the presence of either Ca or Mg ions enhances the

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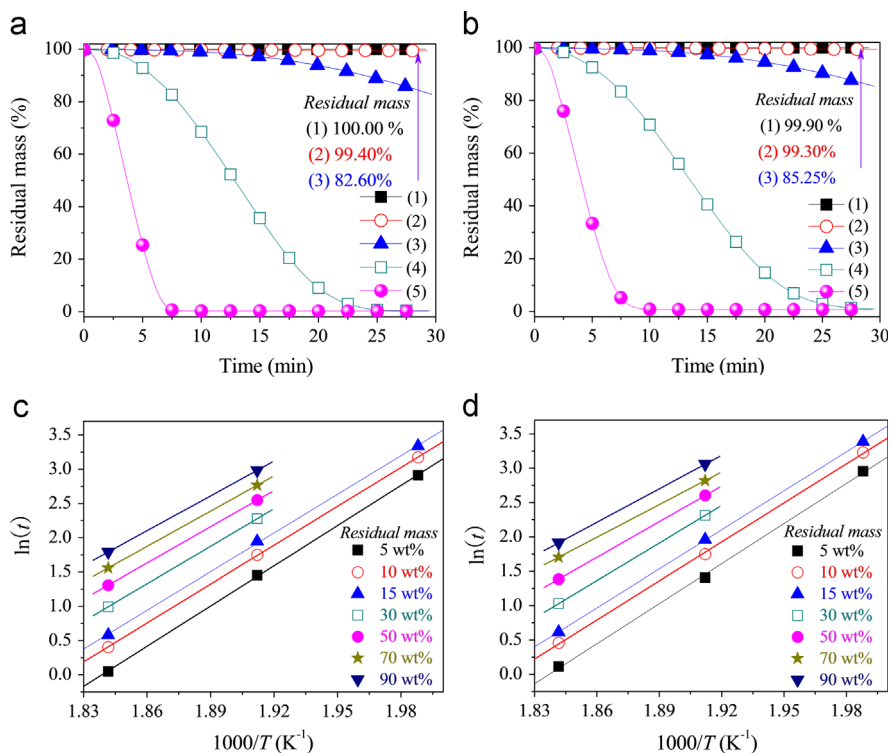E-mail address: zhumf@dhu.edu.cn (M. Zhu).

Fig. 1. Isothermal TG curves of PHBV in (a) nitrogen atmosphere and (b) air atmosphere at (1)180 °C, (2) 210 °C, (3) 230 °C, (4) 250 °C and (5) 270 °C. the corresponding activation energy plots for isothermal weight loss in (c) nitrogen atmosphere and (d) air atmosphere.

depolymerization of P(3HB) molecules, whereas Zn ions hardly catalyze the reaction [17]. Up to now, even though many research works have been carried out on the subject of PHAs thermal degradation, a clear description for the whole thermal degradation process and decomposition mechanisms has not yet been provided.

In this study, the thermal degradation process and decomposition mechanisms of PHBV have been studied under isothermal conditions. A more detailed description of the changes in the molecular chain structure during the thermal degradation process provides the theory basis for bio-based polyesters modification.

2. Experimental

2.1. Materials

PHBV with 1.05 mol% 3-hydroxyvalerate (3HV) ($M_n = 1.16 \times 10^4$ g mol^{-1}, $PDI = 2.30$) was supplied by Tianan Biologic Material Co., Ltd. (Ningbo, China). Dichloromethane and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Measurements

The temperature-dependent profile of weight loss was investigated by using a thermal gravimetric analysis (TG 209 F1 Iris, NETZSCH, Germany). The isothermal degradation of samples was carried out under nitrogen or air atmosphere at 180 °C, 195 °C, 210 °C, 230 °C, 250 °C and 270 °C,

respectively. The obtained solid residues were analyzed with ^{1}H NMR and GPC techniques. ^{1}H NMR analyses of samples were carried out by using a Bruker AC-400NMR spectrometer with tetramethylsilane as an internal standard [18]. Molecular weight analysis was carried out by using a Waters Instrument (USA) with a Waters 1515 apparatus. The type and relative amount of residual metal ions in PHBV raw material were measured by using a Leeman Prodigy inductively coupled plasma-optical emission spectroscopy (ICP-OES, Hudson, NH, USA). The composition and its chemical structure of volatile gases were investigated by using a pyrolysis-gas chromatography-mass spectrometry at 240 °C and 290 °C.

3. Results and discussion

3.1. Temperature-dependent profiles of weight loss

Polymers can be degraded by exposure to high temperature, oxygen, moisture and radiation, etc. Often, the multiple factors can result in the accelerated depolymerization. In order to evaluate the influences of the temperature and environmental atmosphere on the weight loss of PHBV, the measuring parameters such as residual mass, molecular weight were obtained by TG and GPC techniques. Moreover, according to Maccallum et al. [19,20], the activation energy (ΔE_{td}) was estimated depending on the weight loss by using the following equation,

$$\ln(t) = \ln\left[F\left(1 - \frac{X}{100}\right)\right] - \ln(A) + \frac{\Delta E_{td}}{RT} \qquad (1)$$