

Crystallization kinetics, morphology, and hydrolytic degradation of novel biobased poly(butylene succinate-co-decamethylene succinate) copolyesters



Xun Dai ^{a, b}, Zhaobin Qiu ^{a, *}

^a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

^b Engineering Laboratory of Chemical Resources Utilization in South Xinjiang of XPCC, Tarim University, Alar 843300, China

ARTICLE INFO

Article history:

Received 16 December 2016

Received in revised form

22 January 2017

Accepted 28 January 2017

Available online 31 January 2017

Keywords:

Biodegradable

Poly(butylene succinate)

Copolyesters

Crystallization kinetics

Morphology

Hydrolytic degradation

ABSTRACT

In previous work, we synthesized three novel biodegradable poly(butylene succinate-co-decamethylene succinate) (PBDS) copolyesters with different decamethylene succinate (DS) compositions and studied their basic thermal behaviors, crystal structure, and mechanical properties (Polym. Degrad. Stab. 134 (2016) 305–310). In this work, the isothermal melt crystallization kinetics, spherulitic morphology and growth rates, and hydrolytic degradation of these PBDS copolyesters were further investigated and compared with those of their homopolymer poly(butylene succinate) (PBS). With increasing DS composition and crystallization temperature, the overall isothermal melt crystallization rates of PBDS decreased; however, the crystallization mechanism of PBDS and PBS remained unchanged. Spherulitic morphology and growth rates of PBDS and PBS were investigated in a wide range of crystallization temperatures. Increasing crystallization temperature and DS composition decreased growth rates of PBDS spherulites. Both PBDS and PBS exhibited a crystallization transition from regime II to regime III; moreover, the crystallization regime transition temperature shifted to lower temperature with increasing DS composition. The hydrolytic degradation rates of PBDS copolyesters gradually decreased with increasing DS composition. Scanning electron microscopy study demonstrated the surface erosion mechanism of the hydrolytic degradation of PBDS and PBS.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

From the viewpoints of both resource and environment, biodegradable polymers have attracted considerable attention to resolve the problems arising from traditional polymeric materials [1–3]. Poly(butylene succinate) (PBS) is a promising linear aliphatic polyester because of its relatively high melting temperature, favorable biodegradability, and good mechanical properties [4,5]. The melting temperature of PBS is about 114 °C; moreover, PBS has relatively good mechanical properties similar to those of polypropylene and polyethylene [4]. The synthesis, crystallization kinetics, morphology, mechanical properties, and biodegradable degradation of PBS have been extensively investigated [6–17]. Blending and copolymerization have often been utilized to improve the properties of PBS for extending its wider practical applications.

Many polymers have been used to blend with PBS, such as poly(ethylene oxide), poly(vinylidene fluoride), poly(vinyl phenol), poly(ϵ -caprolactone), poly(lactic acid), and poly(ethylene succinate) [10,18–25]. Several PBS based copolyesters have been successfully prepared by incorporating the third novel monomer into the backbone of PBS to modify the chemical structure and adjust the physical properties of PBS, such as poly(butylene succinate-co-ethylene succinate), poly(butylene succinate-co-butylene adipate), poly(butylene succinate-co-butylene terephthalate), poly(butylene succinate-co-propylene succinate), and poly(butylene succinate-co-hexamethylene succinate) [26–32].

In previous work, we successfully synthesized three novel poly(butylene succinate-co-decamethylene succinate) (PBDS) copolyesters and its homopolymer PBS with high molecular weights from the biobased monomers [33]. The chemical structure, basic thermal behaviors, crystal structure, and mechanical properties of PBDS with different decamethylene succinate (DS) compositions were extensively investigated and compared with those of PBS. Both PBDS and PBS displayed high thermal stability and the same

* Corresponding author.

E-mail address: qiuzb@mail.buct.edu.cn (Z. Qiu).

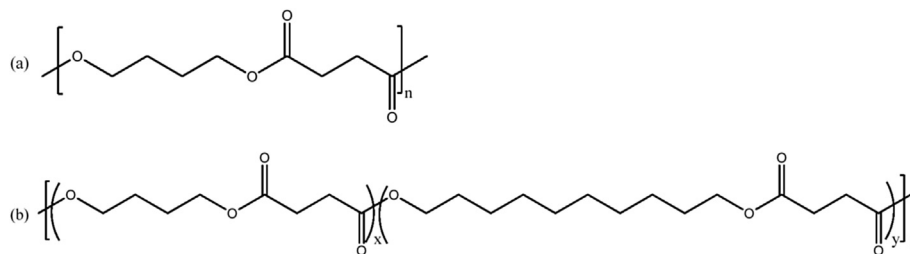


Fig. 1. Chemical structures of (a) PBS and (b) PBDS.

Table 1

Compositions, molecular weights, glass transition temperatures (T_g), melting point temperatures (T_m), and equilibrium melting temperatures (T_m^0) of PBS and PBDS.

Samples	BS/DS (molar ratio)	M_w (g/mol)	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_m^0 ($^{\circ}\text{C}$)
PBS	100/0	1.16×10^5	-32.8	113.1	132.2
PBDS12	88/12	9.93×10^4	-40.9	102.6	122.2
PBDS23	77/23	1.04×10^5	-46.7	92.0	113.6
PBDS33	67/33	1.34×10^5	-49.2	80.4	109.9

PBS-type crystal structure, but PBDS showed smaller crystallinity than PBS. With increasing DS content, the nonisothermal melt crystallization peak temperature, glass transition temperature, melting temperature, and equilibrium melting temperature of PBDS copolyesters gradually decreased. The well-known Flory equation may well describe the composition dependence of melting temperature of PBDS copolymers. The mechanical properties of PBDS could be adjusted by changing DS composition to meet different practical requirements.

As crystallization behavior may affect the aggregation structure of polymers, which in turn further affects the materials performance, it is necessary to study the crystallization kinetics and morphology of PBDS copolyesters. In this work, we studied not only the crystallization kinetics and morphology but also the hydrolytic degradation of PBDS and PBS to better understand the effect of different DS compositions. The research results reported herein should be interesting and helpful to better understand the structure and properties relationship of these novel biobased PBS based copolymers and may promote the potential application.

2. Experimental section

2.1. Materials

PBDS copolyesters and PBS were successfully synthesized in our laboratory through a two-step esterification and polycondensation process [33]. Fig. 1 shows their chemical structures. The detailed data of all samples were determined in previous work and are listed in Table 1 [33].

2.2. Characterizations

The isothermal melt crystallization kinetics study of PBDS and PBS was performed with a TA Instrument differential scanning calorimeter (DSC) Q100 under nitrogen atmosphere. The samples were first heated to 140 $^{\circ}\text{C}$ from room temperature at 20 $^{\circ}\text{C}/\text{min}$, held there for 3 min to erase any previous thermal history, subsequently quickly cooled to the desired crystallization temperature (T_c) at 60 $^{\circ}\text{C}/\text{min}$, and crystallized isothermally for a certain period of time to ensure complete crystallization.

The spherulitic morphology and growth of PBDS and PBS were measured with a polarized optical microscope (POM) (Olympus

BX51) equipped with a temperature controller (Linkam THMS 600). The thermal treatment of the sample for POM experiment was the same as that for DSC test.

To study the degradation behavior, the films of PBDS and PBS were first pressed at 140 $^{\circ}\text{C}$ for 5 min and then quenched into ice water, which were further cut into small specimens with dimensions of about 10 mm \times 10 mm \times 1 mm. The degradation conditions were as follows: the pH value of sodium hydroxide (NaOH) solution was 14, the temperature was 37 $^{\circ}\text{C}$, and the shaking speed was 150 rpm. After a period of time of degradation, the films were washed with deionized water to neutral and dried

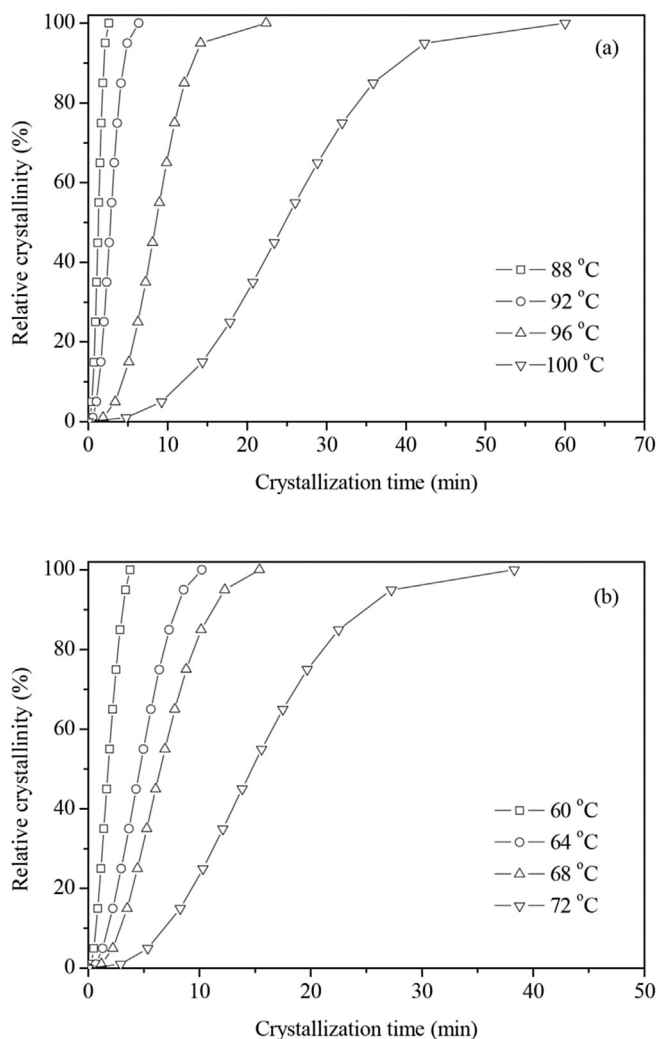


Fig. 2. Development of relative crystallinity with crystallization time at indicated T_c values for (a) PBS and (b) PBDS23.

Download English Version:

<https://daneshyari.com/en/article/5200817>

Download Persian Version:

<https://daneshyari.com/article/5200817>

[Daneshyari.com](https://daneshyari.com)