Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–8

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Thermal degradation behaviors and biodegradability of novel nanocomposites based on various poly[(butylene succinate)-co-adipate] and modified layered double hydroxides

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ARTICLE INFO

Article history:
Received 2 September 2016
Revised 10 April 2017
Accepted 24 April 2017
Available online xxx

Keywords:
Poly[(butylene succinate)-co-adipate] (PBSA)
Layered double hydroxide (LDH)
Nanocomposites
Degradation

ABSTRACT

Synthesized via a polycondensation reaction, three biodegradable poly[(butylene succinate)-co-adipate] (PBSA) containing various succinic acid (SA) and adipic acid (AA) ratios were combined with an organically modified layered double hydroxide (m-LDH) to manufacture PBSA/m-LDH nanocomposites. The structures of these PBSA/m-LDH nanocomposites were studied via wide-angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). The WAXD and TEM analyses demonstrated that the various nanocomposites formed with exfoliated LDHs were effectively dispensed in the PBSA matrix. The effects of m-LDH on the biodegradation of PBSA/m-LDH nanocomposites were explored using lipase from *Pseudomonas fluorescens*. The degradation rates of the neat PBSA copolymers decrease in the order PBSA-25 > PBSA-50 > PBSA-75. The faster degradation rate of PBSA-25 is a consequence of the lower melting temperature and flexibility of its chain backbone. Moreover, weight loss decreases with increasing loading of m-LDH, suggesting that the presence of m-LDH hinders the degradation of the PBSA copolymers. On the basis of the molecular weight and polydispersity index of the remaining PBSA-based specimens, we propose that the degradation behavior of PBSA using *P. fluorescens* lipase is controlled by exo-type hydrolysis activity wherein PBSA copolymer degradation arises from both ends of the polymer chains.

1. Introduction

In recent years, several studies have focused on developing biodegradable polymers for ecological purposes. One of the most interesting biodegradable polymers is poly[(butylene succinate)-co-adipate] (PBSA) [1–12]. PBSA is a synthetic aliphatic copolyester and is synthesized via polycondensation of 1,4-butanediol in the presence of succinic and adipic acids [1–3]. Compared to the degradation rate of poly(butylene succinate) (PBS), with that of PBSA is higher because of its flexible macromolecular chains and lower crystallinity [7]. The addition of an inorganic layered material, such as montmorillonite and a layered double hydroxide (LDH), to biodegradable polymers has been shown to reduce these disadvantages [6,13–24].

LDHs are a group of two-dimensional inorganic substances with a lamellar structure. LDHs have drawn tremendous attention because they are available in numerous sizes and shapes. Several studies have focused on polymer/LDH nanocomposites, which substantially enhance the polymer structure's physical properties after intercalation and exfoliation within the polymer structure [6,13–19]. Because of the strong electrostatic interactions between the hydroxide layers, the polymer chains are not easy to intercalate into the interlayer gallery of LDHs. To overcome this difficulty, researchers have used organomodifiers to delaminate LDH [6,13–22]. For green products, biocompatible and nontoxic organomodifiers have become an emphasized research topic. In the present study, biocompatible sorbitol and oleic acid are used as organomodifiers to manufacture modified LDHs (m-LDHs) via one-step coprecipitation. In our previous research, we demonstrated that the incorporation of m-LDHs into the PBSA polymer matrix with the feed molar ratios of succinic acid/adipic acid = 75/25 can result in PBSA/m-LDH nanocomposites with improved crystallization behavior [13].

Previous studies have mostly focused on the nonisothermal crystallization, microstructure, and rheological behavior of PBSA combined with various inorganic layered materials [4,7–11]. Therefore, in the present study, we used a two-stage polycondensation reaction to synthesize various compositions of PBSA copolymers [1–3,13]. The dispersion, thermal degradation behavior, and

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http://dx.doi.org/10.1016/j.jtice.2017.04.036
1876-1070/

Table 1
Composition and molecular weight of synthesized polyesters.

Polymer	Feed ratio [SA]/[AA] (mol%)	Polymer ratio[a] [SA]/[AA] (mol%)	M_w (g/mol) × 10^4	M_n (g/mol) × 10^4	PDI	T_m (°C)	X_c[b] (%)
PBSA-75	75/25	73.17:26.83	3.4	1.9	1.79	101.5	52.19
PBSA-50	50/50	49.57:50.43	3.4	1.8	1.88	53.4	30.83
PBSA-25	25/75	26.37:73.63	2.0	1.2	1.66	33.5	42.18

[a] Composition measured by ^{1}H NMR.
[b] X_c was calculated by dividing the observed heat of fusion from the melting endotherm by the theoretical value (113.4°J/g) for a 100% crystalline PBSA (from 100/0 to 51/49 of copolymer composition) and by the theoretical value (135.5°J/g) for a 100% crystalline PBSA (from 38/62 to 0/100 of copolymer composition).

biodegradability of the various PBSA/m-LDH nanocomposites were examined.

2. Materials and methods

2.1. Materials

Oleic acid, $Al(NO_3)_3•9H_2O$ (98%), and $Mg(NO_3)_2•6H_2O$ (97%) were purchased from Showa Chemicals Corp. Adipic acid (AA), lipase from *P. fluorescens*, sorbitol, and titanium(IV) isopropoxide were acquired from Sigma-Aldrich Chemical Company. Succinic acid (SA) and chloroform were obtained from J.T. Baker Chemical Company. All chemicals were used as received.

2.2. Sample preparation

2.2.1. Synthesis of various PBSA/m-LDH nanocomposites

Three types of PBSA were synthesized using an identical process, which has been described elsewhere [1–3,13]. The feed molar ratios of [SA] to [AA] were 25:75, 50:50, and 75:25; the resulting products are hereinafter referred to as PBSA-25, PBSA-50, and PBSA-75, respectively. The feed compositions and molecular weights of the various PBSA copolymers are given in Table 1. LDH and m-LDH powders were fabricated as indicated by the methods described in our previous investigations [13,14].

Various PBSA/m-LDH nanocomposites were fabricated according to our previously reported method [13]. The nanocomposite samples are labeled as *x* wt% PBSA/m-LDH, where *x* wt% is the weight percent of m-LDH.

2.2.2. Enzymatic degradation

All samples (10 mm × 10 mm) were placed in 24-well plates with 1 ml of 0.1 M phosphate buffer, pH 7.4, containing 1 mg of lipase from *P. fluorescens*. Enzyme solutions were maintained at 37 °C in a constant temperature bath. The duration of the biodegradation depends on the time required for complete degradation of the neat copolymers. The weight loss W_{loss} (%) of all samples as a result of this process was calculated using the expression W_{loss} (%) = 100[($W_0 - W_t$)/W_0], where W_0 is the initial weight and W_t is the weight after biodegradation.

2.3. Wide-angle X-ray diffraction (WAXD)

The WAXD experiment equipped with a Ni-filtered Cu Kα radiation source ($\lambda = 1.542$ Å) were recorded with a Bruker D8 advance diffractometer; the samples were scanned at a rate of 1°/min over the 2θ range $1.5° \leq 2\theta \leq 40°$.

2.4. Transmission electron microscopy (TEM)

TEM images of all nanocomposites were obtained on a Hitachi HF-2000 operated at an accelerating voltage of 200 kV. The samples obtained at room temperature were ultrathin-sectioned via Reichert Ultracutultramicrotome equipped with a diamond knife.

2.5. Nuclear magnetic resonance (NMR)

The ^{1}H NMR spectrum of specimen was collected with a Varian Inova NMR spectrometer at a proton resonance frequency of 600 MHz. $CDCl_3$ was used as the solvent and internal standard.

2.6. Field-emission scanning electron microscopy (FESEM)

Field-emission scanning electron microscopy (FESEM; JEOL JSM-6700F) was used to evaluate the fracture surface of the nanocomposites. The acceleration voltage was 3 kV, and the surfaces of all samples were sputter coated with gold to avoid charging.

2.7. Thermogravimetric analysis (TGA)

The thermal behavior was determined using a PerkinElmer TG/DTA 6300 thermogravimetric analyzer. All specimens were scanned under a nitrogen atmosphere from 30 °C to 800 °C at a heating rate of 10 °C/min.

2.8. Differential scanning calorimetry (DSC)

The melting point of three neat copolymers was studied using a PerkinElmer Pyris Diamond differential scanning calorimeter calibrated using indium. The three neat copolymers were heated from 25 °C to 100 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.9. Gel permeation chromatography (GPC)

The number-average molecular weight M_n, weight-average molecular weight M_w, and polydispersity PDI = M_n/M_w of the resulting polymers were measured by gel permeation chromatography (GPC; Waters 717 Plusautosampler, Waters Instruments, Rochester, NY, USA). Calibration was performed using polystyrene standards with narrow molecular-weight distributions.

3. Results and discussion

3.1. Synthesis and structure of various PBSA copolymers

Various compositions of PBSA copolyesters (*i.e.*, copolyesters with different moleratios of [SA] and [AA]) were analyzed via ^{1}H NMR spectroscopy. For simplicity, only the ^{1}H NMR data of the PBSA-25 copolymer is revealed in Fig. 1. As shown in this figure, the signals at $\delta = 4.13$, 2.63, and 2.33 ppm correspond to $OOCH_2^-$ for the 1,4-butanediol component, $COCH_2^-$ for the succinyl group, and $COCH_2^-$ for the adipoyl unit, respectively [1–3,13]. The chemical composition of PBSA-25 copolyester was determined using the area ratio of the peak at $\delta = 2.63$ ppm to that at δ 2.33 ppm; the results are presented in Table 1. The ratio of succinyl unit to adipoyl units is approximately equal to the feed ratio of [SA] to [AA], indicating that the compositions of the prepared copolyester are consistent with those estimated on the basis of the feed proportions.

Please cite this article as: Y.-A. Chen et al., Thermal degradation behaviors and biodegradability of novel nanocomposites based on various poly[(butylene succinate)-co-adipate] and modified layered double hydroxides, Journal of the Taiwan Institute of Chemical Engineers (2017), http://dx.doi.org/10.1016/j.jtice.2017.04.036