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Synthesis, physical properties and enzymatic degradation of bio-based poly(butylene adipate-co-butylene furandicarboxylate) copolyesters

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ABSTRACT

A series of bio-based poly(butylene adipate-co-butylene furandicarboxylate) (PBAFs) copolyesters were synthesized from 2,5-furandicarboxylic acid (FDCA), adipic acid (AA), and 1,4-butanediol (BDO) through a two-step polycondensation reaction. The copolyesters were characterized by ^{1}H NMR, GPC, DSC, XRD and tensile tests, and their enzymatic degradation behaviors were also investigated. They were random copolymers whose composition was well controlled and the weight average molecular weight (M_w) ranged from 54,100 to 76,800 g/mol. By combining the results of DSC and XRD, with increasing FDCA content, PBAFs changed from semi-crystalline polymers to nearly amorphous polymers, then to semi-crystalline polymers again. Specifically, the crystallizability and melting temperature (T_m) decreased with FDCA content 0–50 mol%, but rose again at FDCA content 75–100 mol%. And, the glass transition temperature (T_g) increased continuously with increasing FDCA content. Consequently, the tensile modulus and strength decreased but the ultimate elongation increased at lower FDCA content (0–50 mol %), which were converse at higher FDCA content (75–100 mol%). Especially, the P(BA-40 mol% BF) shows outstanding elasticity and rebound resilience. In addition, the influences of FDCA content on the enzymatic degradation by lipase from porcine pancreas were studied in terms of the weight loss and morphological change. At FDCA content of 0–50 mol%, the copolyesters showed biodegradability but only the degradation rate of P(BA-10 mol% BF) was faster than PBA. When the FDCA content were 75–100 mol%, they were actually un-degradable. Thus, depending on their composition, PBAFs might find applications from biodegradable elastomers to thermoplastics.

1. Introduction

Recently, bio-based plastics have attracted widespread attention due to the oil shortage, global warming and environmental pollution. By definition, bio-based plastics are the plastics derived from renewable resources (such as starch, cellulose, protein, etc.), carbon dioxide, and biopolymers (such as polysaccharide, polyester, polyisoprene, etc.). Currently, the well-known bio-based plastics mainly include the starch-based plastics, cellulose-based plastics, poly(lactic acid) (PLA), poly(hydroxyl alkanoates) (PHAs), etc. Meanwhile, other kinds of bio-based plastics have been developed that lead to many commercial products, such as bio-based polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyamide (PA) and so on [1–3].

Different types of bio-based plastics can be synthesized via different bio-based platform monomers. Since 2004, U.S. Department of Energy has screened 12 kinds of bio-based platform monomers as the most important building blocks or top value-added chemicals. Among them, 2,5-furandicarboxylic acid (FDCA) is a bio-based aromatic diacid monomer, which can be produced from cellulose or semi-cellulose through a multistep process including bioconversion, dehydration, and oxidation in which hexose and 5-hydroxymethylfurfural are important intermediates [4–6]. The physical and chemical properties of FDCA are close to those of terephthalic acid (TPA), which is the world's largest output of dicarboxylic acid. Thus, lots of work has concentrated on developing FDCA-based plastics in order to replace TPA-based plastics.

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Aliphatic polyesters, as the largest class of TPA-based plastics, have included many industrially important products such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) and poly (trimethylene terephthalate) (PTT). Motivated by sustainable chemical industry, significant activity exists in developing FDCA-based polyesters recently. For example, poly(ethylene 2,5-furandicarboxylate) (PEF) and poly(butylene 2,5-furandicarboxylate) (PBF) have been synthesized and shown better performance in some areas compared with TPA-based analogues. Meanwhile, studies on the polymerization of FDCA with different diols have also been reported [7–13].

Aliphatic-aromatic copolyesters, as the second largest class of TPA-based plastics, have been developed into many novel products such as the well-known poly(butylene adipate-co-butylene terephthalate), who has been commercialized under the trademarks of Ecoflex® and Easter-bio® by BASF and Eastman Chemical respectively, and a tunable balance between the biodegradation and desirable physical properties was successfully achieved [14,15]. Therefore, it will be very interesting to incorporate FDCA into aliphatic polyesters instead of TPA targeting bio-based and biodegradable copolyesters. So far, despite its importance, there have been only a few studies reporting FDCA-based copolyesters of poly(butylene succinate-co-butylene furandicarboxylate) (PBSF) and poly(ethylene succinate-co-ethylene furandicarboxylate) (PESF) [16,17], and there is no report on the enzymatic degradation behaviors of FDCA-based copolyesters.

Thus, our aim is to synthesize a series of poly(butylene adipate-co-butylene furandicarboxylate) (PBAFs) copolyesters and study the influences of FDCA on the physical properties and enzymatic degradation behaviors of the copolyesters. In this work, we have synthesized the PBAFs via an esterification and polycondensation process using the tetrabutyl titanate as catalyst. They are characterized by GPC, ^{1}H NMR, DSC and TGA, and the tensile properties and enzymatic degradation are also evaluated. We have found that PBAFs range from thermoplastics to elastomers depending on their composition. Besides, the biodegradability of the copolyesters is controllable by the adjustment of the FDCA content.

2. Experimental methods

2.1. Materials

2,5-furandicarboxylic acid (FDCA) with the purity of 99.7% was kindly supplied by Algal Energy and Bio-based Product Group. Adipic acid (AA), 1,4-butanediol (BDO), tetrabutyl titanate (TBT), polyphosphoric acid (PPA) and other reagents were analytically pure and purchased from Aladdin Reagent Co. Ltd and used as received. Lipase from porcine pancreas (30–90 units/mg) was purchased from Sigma–Aldrich Co. Ltd.

2.2. Synthesis of PBAFs

The synthesis of poly(butylene adipate-co-butylene furandicarboxylate) (PBAFs) was performed via a two-stage melt polycondensation adapted as: esterification at atmospheric pressure and polycondensation at reduced pressure. According to the molar percentage of FDCA in feed, the PBAFs were labeled as PBAF10, PBAF20, PBAF30, PBAF40, PBAF50 and PBAF75. For synthesis of PBSF10-75, FDCA, AA, BDO (diol/diacid molar ratio 1.5:1), TBT (0.5 mmol/mol diacid) (TBT is proved to significantly accelerate the esterification reaction of aromatic dicarboxylic acid) and PPA (0.5 mmol/mol diacid) (PPA is believed to prevent side reactions such as etherification and thermal decomposition) were added into a four neck round bottom flask and equipped with a mechanical stirring [18,19]. In the first step, the esterification reaction was conducted at 190–210 °C for 4 h with a N_2 inlet. In the second step, another part of TBT (1 mmol/mol diacid) was added, and the polycondensation reaction was conducted at 220–250 °C for 4 h under a reduced pressure of 10 Pa. For PBA and PBF, they also synthesized using the same procedure.

Table 1
Molecular characteristics of PBA, PBAFs and PBF.

Sample	^{1}H NMR	GPC		
	BF mol% in copolyesters	M_n	M_w	DI
PBA	0.0	36,800	61,500	1.67
PBAF10	90.2	41,300	76,800	1.86
PBAF20	80.0	33,900	58,300	1.72
PBAF30	69.9	26,400	55,700	2.11
PBAF40	60.1	32,300	64,000	1.98
PBAF50	49.8	28,500	54,100	1.90
PBAF75	24.9	31,300	69,800	2.23
PBF	100.0	Not determined	Not determined	Not determined

2.3. Characterization

The molecular weight was determined by a Waters gel permeation chromatography (GPC). Chloroform was used as solvent and polystyrene standards were used for calibration. The molecular weight of PBF was not measured because its insolubility in chloroform.

The ^{1}H NMR spectra were recorded on a Bruker AMX-300 apparatus, using chloroform-d ($CDCl_3$) as solvent of PBA and PBAFs, and trifluoroacetic acid-d (CF_3COOD) for PBF.

Differential scanning calorimetry (DSC) measurements were carried out with a Mettler Instrument under nitrogen follow. A heat/cool/heat procedure was used to avoid the influences of thermal histories that starting from −50 °C and going up to 200 °C at a rate of 10 °C/min.

The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 focus, using Cu-Kα radiation in the scan ranged from 5 to 60° in 2θ with steps of 0.02° at fixed counting time of 4 s.

Tensile tests were done with Instron tester in accordance with ASTM D638. The dumbbell-shaped samples of 25 mm length, 4 mm width, and 2 mm thickness were made by melt-pressing using a hot press at 30 MPa for 30 s and the temperatures ranged from 100 °C to 190 °C above their melting temperatures. Then the samples were stretched at 25 °C with a 50 mm/min stretching rate. At least five specimens were tested for each sample, and the average values are reported.

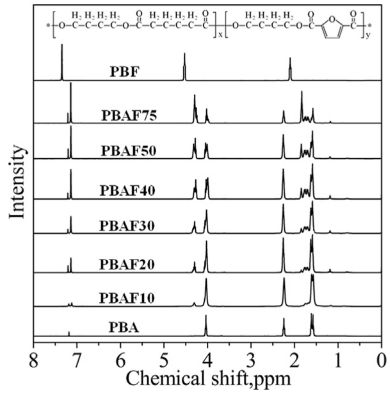

Fig. 1. ^{1}H NMR spectra of PBA, PBAFs and PBF.