



Biobased poly(butylene 2,5-furandicarboxylate) and poly(butylene adipate-co-butylene 2,5-furandicarboxylate)s: From synthesis using highly purified 2,5-furandicarboxylic acid to thermo-mechanical properties



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ABSTRACT

To synthesize high quality (co)polyesters derived from 2,5-furandicarboxylic acid (FA), an acetic acid refluxing/pH-swing method was proposed to purify FA. 2-Carboxyl furfural and other impurities were removed completely from FA with this method. Using highly purified FA, biobased polyester poly(butylene furandicarboxylate) (PBF) and aliphatic-aromatic copolyesters poly(butylene adipate-co-butylene 2,5-furandicarboxylate)s (PBAFs) were synthesized via melt (co)polycondensation. The (co)polyesters were characterized with GPC, FTIR, ¹H NMR, DSC and TGA, and their tensile mechanical properties were also assessed. The copolyesters possess random chain structure, monomer feed ratio-controlled copolymer composition and excellent thermal stability ($T_{d,5\%} > 340$ °C) in full composition range. Both BA-rich and BF-rich PBAFs are crystalline polymers. The crystallizability decreases with composition, up to nearly amorphous at moderate ϕ_{BF} (40–60%). PBAFs with ϕ_{BF} no more than 50% exhibit obvious high-elastic deformation and rebound resilience, and possess tensile properties (E 18–160 MPa, σ_b 9–17 MPa, ϵ_b 370–910%) comparable to poly(butylene adipate). PBAFs with higher ϕ_{BF} behave like nonrigid plastics with low tensile moduli (42–110 MPa), moderate strength (30–42 MPa) and high elongation at break (310–470%). In comparison, PBF is a strong and tough thermoplastic having balanced mechanical properties, namely, much higher tensile modulus (1.9 GPa) and strength (56 MPa) and high elongation at break (260%). It seems necessary and effective to use highly purified FA for synthesizing high performance FA-derived (co)polyesters.

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1. Introduction

As replacement of polymers derived from fossil resources, polymers based on bio-renewable resources have drawn worldwide attention from both academia and industry due to the sustained dwindling of fossil resources as well as increasing environmental concerns [1–6]. The burgeoning surge in conversion and utilization of biomass in recent years has offer great opportunities in synthesizing biobased monomers and polymers [2–6]. 2,5-furandicarboxylic acid (FA) is an important biobased monomer, which can be produced in large scale from cellulose or hemicellulose via a multistep process including bioconversion,

dehydration and oxidation [7–10]. Because of its aromatic structure and biobased origin, FA has been highlighted as potential replacement of fossil-based monomers like terephthalic acid (TPA). It has also been screened to be one of the most important biobased building blocks by the U.S. Department of Energy [11]. Therefore FA represents a very promising monomer for new biobased polyesters and other polymers.

In recent years, FA-based polyesters including poly(ethylene furandicarboxylate) (PEF) [12–16], poly(propylene furandicarboxylate) (PPF) [13,15], poly(butylene furandicarboxylate) (PBF) [15–17] and others [17–19] have been reported. These polyesters are deemed as furan counterparts of TPA-based polyesters because they display comparable thermo-mechanical properties. Several aromatic copolyesters derived from FA have also been reported [20,21]. All these aromatic (co)polyesters, like the TPA counterparts, will not be biodegradable. However, aliphatic-aromatic copolyesters of FA,

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aliphatic diacid and diol may be potentially biodegradable within appropriate composition range as they possess chemical structure similar to the well-known biodegradable copolyesters poly(-butylene adipate-co-butylene terephthalate) (PBAT) and poly(-butylene succinate-co-butylene terephthalate) (PBST) [22–24]. In the past two years, the synthesis and thermo-mechanical properties of poly(butylene succinate-co-butylene furandicarboxylate) (PBSF) [25], poly(ethylene succinate-co-ethylene furandicarboxylate) (PESF) [26] and poly(butylene adipate-co-butylene furandicarboxylate) (PBAF, ϕ_{BF} up to 75%) [27] were reported in succession. Indeed, PBAF containing butylene furandicarboxylate unit $\leq 50\%$ is enzyme-degradable by lipase from porcine pancreas [27].

In our previous study [25], we reported the synthesis and mechanical properties of PBSF in full composition range, and found it has tunable thermo-mechanical properties from thermoplastics to elastomers. In this study, we further report the synthesis of PBAF in full composition range using highly purified FA monomer, and the characterization of the relationship between their chain structure and thermo-mechanical properties. High molecular weight PBAFs with particularly excellent thermal stability was successfully synthesized and characterized. It is found that the thermal transition and mechanical properties are also tunable with the copolymer composition.

2. Experimental section

2.1. Materials

Adipic acid (AA, Shanghai Dibo Chem., China), 1,4-butanediol (BDO, Sinopec Yizheng Chem. Fibre, China), tetrabutyl titanate (TBT, $\geq 99.0\%$, Aladdin) and lanthanum(III) acetylacetonate ($\text{La}(\text{acac})_3$, $\geq 99.0\%$, Shandong Haili Chem., China) were all used as received. 2,5-Furandicarboxylic acid (FA, 98%) was purchased from Satar Chem., China. It was purified by a modified method based on the previously reported reflux purification [25]. First, FA, acetic anhydride and deionized water (20:68:32 w:w:w) were mixed under stirring at room temperature for 1 h (Acetic anhydride was hydrolyzed to be acetic acid, so acetic acid can be used too.). The mixture was heated to reflux temperature and kept for 4 h under nitrogen atmosphere, and then filtrated with a Buchner funnel and washed with deionized water for five times. Secondly, the product was dissolved in a NaOH solution (NaOH:FA 1:1 w:w), and then activated carbon (C:FA 0.5:1 w:w) was added. After stirring for 5 h, the mixture was filtrated by a G4 sand core funnel. The filtrate was then acidified by hydrochloric acid until $\text{pH} < 3$. Such pH-swing operation was repeated once. At last, the precipitated white solid was separated by filtration and washed with deionized water for five times. After drying under vacuum to constant weight, highly purified FA was obtained.

2.2. Synthesis of PBAFs

PBAFs were prepared via direct esterification followed by melt polycondensation. The copolyester prepared with molar percentage of FA in diacid feed (ϕ_{FA}) is named as $\text{PBAF}_{\phi_{FA}}$. The molar fraction of butylene furandicarboxylate (BF) repeating unit in the copolymer (ϕ_{BF}) determined by ^1H NMR is defined as the copolymer composition. For PBAFs10–50 and PBA, AA, FA, BDO (diol/diacid molar ratio 2:1) and TBT (0.1 mol% diacid) were added into a 250 mL four-necked round bottom flask equipped with mechanical stirring and N_2 inlet and heated to 200 °C. The esterification reaction was conducted at 200 °C for 1 h, at 210 °C for 2 h, and finally at 220 °C for 1–2 h. Then, $\text{La}(\text{acac})_3$ (0.1 mol% diacid) was added to the esterification product and the mixture was heated to 230 °C. The polycondensation reaction was performed under vacuum (200–400 Pa) at about 240 °C for 2.5–6 h until Weissenberg effect emerged. The resulting products were dried at 60 °C in vacuum oven for 12 h and

stored in a desiccator before characterization. PBAFs60–90 and PBF were synthesized with the same procedure except that a higher diol/diacid ratio was used. Extra BDO was added before the temperature was heated up to 220 °C in the first step. The total ratio was 2.5:1.

2.3. Characterization

The molecular weight distribution (MWD) of PBA and PBAFs10–80 was determined using an Agilent PL 50 gel permeation chromatography (GPC). Chloroform was used as eluent and polystyrene as standard. The sample concentration was about 3 mg/mL, and the eluent flow rate was 1.0 mL/min.

The FTIR spectra were recorded with a Nicolet5700 spectroscopy. Chloroform was used as solvent for PBA and PBAFs10–80, and 1,1,2,2-tetrachloroethane for PBAF90 and PBF. The solution concentration was 5 mg/mL.

The ^1H NMR spectra were recorded with an AC-80 spectroscopy (400M, BRUKER). Deuterated dimethyl sulfoxide (d^6 -DMSO) was used as solvent for FA, deuterated chloroform (CDCl_3) for PBA and PBAFs10–80, and deuterated 1,1,2,2-tetrachloroethane ($\text{C}_2\text{D}_2\text{Cl}_4$) for PBAF90 and PBF. Tetramethylsilane (TMS) was used as internal reference.

The thermal transition were recorded with differential scanning calorimetry (DSC) on a TA-Q200 thermal analyzer using a standard heating-cooling-heating mode. Both heating and cooling rates were 10 °C/min.

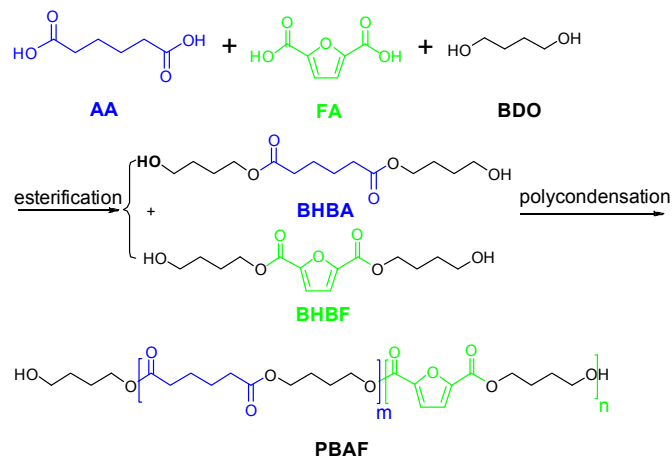
The thermal stability was determined by thermal gravimetric analysis (TGA, PerkinElmer instruments, USA). The samples were measured from 50 °C to 800 °C at 20 °C/min. All measurements were under N_2 atmosphere.

The tensile properties were measured with a Zwick Roell Z020 testing machine at 25 °C according to ASTM D638. Dumbbell-shaped specimens (2 mm in thickness and 4 mm in width) were prepared using a HAAKE MiniJet II Injection moulding machine and then conditioned at 25 °C and 50% relative humidity for over 48 h prior to testing. The crosshead speed was 20 mm/min. For each sample, at least five specimens were tested.

3. Results and discussion

3.1. Synthesis and structure characterization

PBAF copolyesters were synthesized via a two-step esterification-polycondensation procedure shown in Scheme 1. AA and FA



Scheme 1. Synthesis of PBAF copolyesters from BDO, AA and FA via two-step esterification-polycondensation procedure.

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