



Synthesis and characterization of bio-based poly(butylene furandicarboxylate)-b-poly(tetramethylene glycol) copolymers



Weidong Zhou ^a, Yajie Zhang ^b, Ying Xu ^a, Pingli Wang ^a, Li Gao ^a, Wei Zhang ^a, Junhui Ji ^{a,*}

^a National Engineering Research Center of Engineering Plastics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b Algal Energy and Bio-based Product Group, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

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ABSTRACT

Poly(butylene furandicarboxylate)-b-poly(tetramethylene glycol) (PBF-PTMG) copolymers were synthesized from 2,5-furandicarboxylic acid (FDCA), 1,4-butanediol (BDO) and poly(tetramethylene glycol) (PTMG, the M_n is 1000 g/mol) through a process of esterification and polycondensation. The copolymers were characterized by ¹H NMR, GPC, DSC, POM, XRD, TGA and tensile strength measurements. The weight content of PTMG segments in the copolymers was 19.7%, 39.4% and 59.6% respectively, and their M_w ranged from 59,300 to 85,900 g/mol. By combining the results of DSC, POM and XRD, they were block copolymers built up of crystallized PBF segments as the hard blocks and amorphous PBF and PTMG segments as the soft blocks, and the two segments were miscible in amorphous phase. As the content of PTMG segments increased, the glass transition temperature (T_g), the melting temperature (T_m), the crystallization temperature (T_c) and the crystallization ability of these copolymers decreased gradually, while their crystal structure changed little. For mechanical properties, the copolymers exhibited the characteristics of elastomers, showing good stress at break (16–26 MPa) and outstanding elongation at break (381–832%). The copolymers had greatly enhanced elasticity and flexibility properties as the content of PTMG segments increased, and the thermal annealing enhanced their tensile properties due to the more crystallinity and better regularity of PBF segments. Moreover, the TGA results revealed that PBF-PTMG copolymers had excellent thermal stability. Therefore, as novel bio-based copolymers, they might find applications in thermoplastics as well as elastomers.

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1. Introduction

Thermoplastic elastomers are copolymers combining the mechanical properties of the chemically crosslinked elastomers, such as good elasticity and flexibility, with those of conventional thermoplastics, such as great strength and modulus. Furthermore, most of the chemically crosslinked elastomers are thermosets, but thermoplastic elastomers are in contrast relatively easy to use in manufacturing, for example, by injection molding. Hence, thermoplastic elastomers show advantages of both rubbery materials and thermoplastic materials [1,2].

As a novel class of thermoplastic elastomers, thermoplastic copolyester elastomers (TPEE) are copolyesters consisted of short, glassy or crystalline hard segments and long, amorphous soft

segments. In the past few decades, the commercial growth of TPEE has continuously increased due to their unique advantages. Firstly, TPEE with different physical properties can be easily designed by variation of the species of the hard and soft segments and their ratio. Secondly, TPEE have a similar synthetic feature as polyesters, which can be easily synthesized through a process of esterification and polycondensation [3–5]. Generally speaking, in the TPEE, the hard segments are generally aromatic polyesters such as poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT) and poly(butylene terephthalate) (PBT) while the soft segments are polyethers such as poly(ethylene glycol) (PEG) and poly(tetramethylene glycol) (PTMG) [6–8].

Recently, bio-based plastics have attracted great attention due to the oil shortage, global warming and environmental pollution [9,10]. With a big market share of all plastics, aromatic polyesters, such as PET and PBT, urgently need to find their alternatives derived from biomass. Actually, 2,5-furandicarboxylic acid (FDCA), a bio-based aromatic diacid monomer produced from sugars, can be used as a replacement for terephthalic acid (TPA), which is a

* Corresponding author. Postal address: 29, Zhongguancun East Road, Haidian District, Beijing 100190, China. Tel./fax: +86 10 82543432.

E-mail address: jjunhuichina@gmail.com (J. Ji).

petroleum-based monomer used for producing PET and PBT. Lately, significant activities have existed in developing FDCA-based aromatic polyesters such as poly(ethylene 2,5-furandicarboxylate) (PEF) and poly(butylene 2,5-furandicarboxylate) (PBF), which show better performance in some areas compared with TPA-based analogs [11–16].

Inspired by the versatile performance of TPEE, and the great interest in bio-based plastics, and the good performance of FDCA-based polyesters compared with TPA-based polyesters, we think it will be interesting to prepare a novel kind of bio-based TPEE containing FDCA-based polyesters. It is worth mentioning that DuPont™ has developed a bio-based TPEE (Hytre[®] RS, PBT-PTMG copolymers), which contains between 20% and 60% renewably sourced PTMG derived from non-food biomass [17]. In this work, we choose the PBF as the hard segments and PTMG as the soft segments to synthesize the PBF-PTMG copolymers. On the one hand, we can at least modify the physical and mechanical properties of PBF to widen the market potential of the FDCA-based polymers. On the other hand, the PBF-PTMG copolymers might find applications as a novel kind of bio-based TPEE. So far, despite its importance, there is no report on the FDCA-based poly(ester-ether).

Aiming at studying the characterization of the FDCA-based poly(ester-ether), a series of PBF-PTMG copolymers are synthesized from FDCA, 1,4-butanediol and PTMG (the M_n is 1000 g/mol) through a process of esterification and polycondensation using the tetrabutyl titanate as catalyst. The influence of different contents of PTMG segments on the structure, crystallization, thermal and mechanical properties of the copolymers was investigated by ¹H NMR, GPC, DSC, POM, XRD, TGA and tensile strength measurements. Further research about the influence of the molecular weight of PTMG and the other soft segments is under way and will be reported later.

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. 1,4-Butanediol (BDO), tetrabutyl titanate (TBT), poly(tetramethylene glycol) (PTMG) (the molecular weight is 1000 g/mol) and other reagents were analytically pure and purchased from Aladdin Reagent Co. Ltd. and used as received.

2.2. Synthesis of PBF-PTMG

The synthesis of PBF and PBF-PTMG copolymers was performed via a two-stage melt polycondensation adapted as: esterification at atmospheric pressure and polycondensation at reduced pressure. In the first step, calculated amounts of FDCA, BDO (diol/diacid molar ratio 2:1), PTMG (diol/diacid molar ratio 1.05:1), and TBT (0.2 wt% of diacid) were added into a 250 ml four-necked round-bottomed flask equipped with a mechanical stirring. Then the esterification reaction was conducted at 190 °C for 4 h with a N₂ inlet. In the second step, another part of TBT (0.4 wt% of diacid) was added, and the polycondensation reaction was conducted at 240 °C for another 4 h under a reduced pressure of 10 Pa. According to the feed weight content of PTMG, the copolymers were labeled as PBF-PTMG20, PBF-PTMG40 and PBF-PTMG60, respectively.

2.3. Characterization

The molecular weight was determined by a Waters gel permeation chromatography (GPC). Chloroform (CHCl₃) was used as solvent and polystyrene (PS) standards were used for calibration. The

molecular weight of PBF was not measured because its insolubility in CHCl₃.

The ¹H NMR spectra were recorded on a Bruker AMX-300 apparatus, using chloroform-d (CDCl₃) as solvent of PBF-PTMG, and mixed solvent of CDCl₃ and trifluoroacetic acid for PBF. The weight contents of PTMG were calculated by the integral ratios of peaks in the spectra.

DSC measurements were done according to ASTM D3417 with Mettler Instrument under nitrogen. For the melting and melt crystallization behaviors, about 5 mg of sample was measured under a heat/cool/heat procedure from –80 °C to 200 °C at a rate of 10 °C/min. For the glass transitions, about 15 mg sample was measured under a same procedure at a rate of 20 °C/min.

The crystallization morphology was observed by using Polarized Optical Microscopy (POM) (Olympus BX51) coupled with a computer-controlled CCD camera. A hot stage was employed for controlling the temperature. The samples were first melted at 200 °C for 5 min, then they were cooled to 30 °C at a rate of 2 °C/min, and the micrographs were captured at 30 °C.

The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 focus, using Cu-K α radiation in the scan ranged from 5 to 60° with the scanspeed of 0.2 s/° and increment of 0.02°.

Tensile tests were done with Instron tester according to ASTM D638. The dumbbell-shaped specimens of 25 mm length, 4 mm width, and 2 mm thickness were made by melt-pressing using a hot press at 30 MPa and 200 °C. The specimens without annealing were naturally cooled to 25 °C and stored in vacuum for 24 h before tests, while the specimens with thermal annealing were brought to 30 °C below their melting points and maintained for 1 h before cooled. All the specimens were stretched at 25 °C with a 50 mm/min stretching rate.

Decomposition characteristics of the samples were determined with a TA Q50 thermogravimetric analysis (TGA). About 5 mg of each sample was placed in the pan and heated from 25 to 600 °C at a rate of 10 °C/min under the nitrogen atmosphere.

3. Results and discussion

3.1. Molecular weight and chemical structure

Since the physical properties of the PBF-PTMG copolymers depend strongly on their molecular weight and composition, they have been synthesized by a two-stage melt polycondensation from FDCA, BDO and PTMG through the same and efficient process, which can guarantee a relatively high molecular weight and well controlled composition.

The molecular weights were measured by GPC. As listed in Table 1, the number average molecular weight (M_n) ranging from 31,200 to 45,200 g/mol and weight average molecular weight (M_w) ranging from 59,300 to 85,900 g/mol were obtained with dispersity index ($DI = M_w/M_n$) from 1.82 to 2.16, as expected for the synthetic method used.

The chemical structure and weight content of PTMG were characterized by ¹H NMR. In Fig. 1, for all the samples, the CH in the

Table 1
Molecular characteristics of PBF and PBF-PTMG copolymers.

| Sample | ¹ H NMR | GPC | | |
|------------|--------------------|----------------|----------------|----------------|
| | PTMG wt% | M_n | M_w | DI |
| PBF | 0 | Not determined | Not determined | Not determined |
| PBF-PTMG20 | 19.7 | 32,600 | 59,300 | 1.82 |
| PBF-PTMG40 | 39.4 | 45,200 | 85,900 | 1.90 |
| PBF-PTMG60 | 59.6 | 31,200 | 67,400 | 2.16 |

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