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Poly(ethylene 2,5-furandicarboxylate-mb-poly(tetramethylene glycol)) multiblock copolymers: From high tough thermoplastics to elastomers

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HIGHLIGHTS

- P(EF-mb-PTMG) copolymers with high intrinsic viscosity have been synthesized.
- The PTMG segment is partially miscible with PEF and can slightly plasticize PEF.
- PEF-based materials can be tailor-made from high tough thermoplastics to elastomers.
- The presence of PTMG greatly improves toughness while keeping high strength of PEF.
- Supertough (> 50 kJ/m^2) PEF-based materials are reported for the first time.

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ABSTRACT

Poly(ethylene 2,5-furandicarboxylate) (PEF) is a biobased polyester with superior thermo-mechanical and gas barrier properties than poly(ethylene terephthalate) (PET), the most widely used petroleum-based polyester. However, PEF is more brittle than PET. To toughen PEF, a series of P(EF-mb-PTMG) (PETF) multiblock copolymers with high intrinsic viscosity were successfully synthesized via melt polycondensation in the presence of poly(tetramethylene glycol) (PTMG) oligomer diols, and characterized with FTIR, ^{1}H NMR, DSC, WAXD, TGA and SEM, and assessed with tensile and impact testing. The presence of PTMG contributes to promote intrinsic viscosity growth and depress etherification and discoloration side reactions. The PTMG flexible segments show chain length dependent partial miscibility with PEF hard segments, and its presence also plasticizes and promotes cold crystallization of PEF segments. With tuning the PTMG content, high performance PEF-based materials can be tailor-made from high tough thermoplastics with excellent ductility and impact toughness to thermoplastic elastomers with high strength. Particularly, PET^{1K}F-20 shows excellent ductility (elongation at break 252%) while retaining high modulus (3.0 GPa) and yielding strength (74 MPa), and PET^{1K}F-35 is the first PEF-based material with impact strength over 50 kJ/m^2 to date.

1. Introduction

Nowadays, the excessive utilization and discarding of polymeric materials based on petroleum resources have caused growing concerns about depletion of nonrenewable resources and environmental pollution [1–4]. As a typical instance, poly(ethylene terephthalate) (PET) has been produced at huge scale (over 50 million metric tons per year) and becomes the polyester most widely used in fibers, bottles, films and packaging materials in the past decades due to its optical clarity, barrier properties, tensile properties and competitive performance-to-cost ratio [5]. Although PET can be recycled to some extent, however, it inevitably becomes one of the major resources of polymer wastes [6]. On the other hand, relatively high oxygen and carbon dioxide permeability of PET limits its applications in gas-sensitive packages for food and beverage.

2,5-furandicarboxylic acid (FDCA) is a diacid monomer with rigid aromatic ring originated from biomass such as starch, cellulose or hemicellulose [7]. It has physical and chemical properties similar to the

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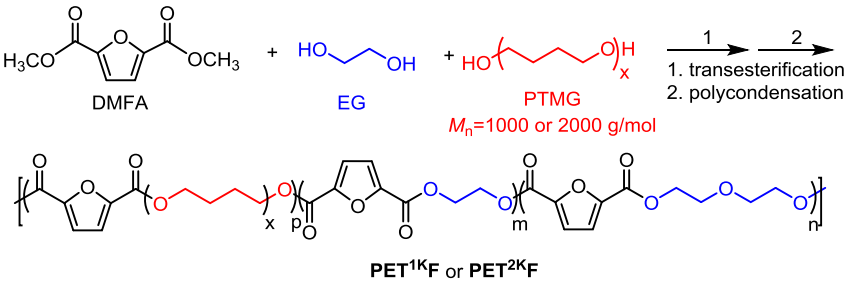

Scheme 1. Schematic diagram of synthesis of P(EF-mb-PTMG) (in abbr., PETF) copolymers.

petro-based monomer terephthalate acid (TPA). Polyesters synthesized from FDCA and various diols have attracted extensive attention in the last decade due to the biobased nature and possibly better properties or higher performance [8–15]. Among them, a lot of attention has been paid to poly(ethylene 2,5-furandicarboxylate) (PEF), a fully biobased polyester synthesized from FDCA or its diester and ethylene glycol (EG). In comparison with PET, it has not only higher glass transition temperature, higher tensile strength and modulus and lower melt processing temperature, but also about one order higher oxygen [16] and carbon dioxide [17] barrier performance as well as reduced environmental impacts during production [18]. These features make PEF a perfect biobased substitute of PET for high-demanding application, especially for high gas barrier applications.

However, PEF has inherent shortcomings, which limits its processing and applications, including very slow melt crystallization rate [10,19] and brittleness [20–23]. PEF shows poor ductility and impact toughness, which may result from its chain stiffness [28]. According to previous reports, it is more brittle than PET, showing elongation at break ranging 1–5% [15,20–27] and notched Izod impact strength around 3.1 kg cm/cm [20]. In order to obtain PEF materials with satisfactory performance, physical and chemical modifications of PEF, including nanocomposite [29,30], blending [31–33], random [20,21,24–26,34–37] and block [26] copolymerization have been frequently reported in the recent literature.

Terzopoulou et al. [35] and Ma et al. [37] reported the synthesis and properties of random copolyesters of PEF containing short chain diacid or diol unit, namely succinic acid and butanediol, but did not report the mechanical properties. Wang et al. [24] reported poly (ethylene sebacate-co-2,5-furandicarboxylate) (PESeF) as a random copolyester containing flexible sebacate units, but the modulus and strength decreased remarkably at low sebacate content and the elongation at break was not improved until high sebacate content (70 mol %) was used. In contrast, random copolyesters of PEF containing rigid units such as terephthalate [27], 1,4-cyclohexylene dimethylene [20,21] or 2,2,4,4-tetramethyl-1,3-cyclobutanediol [25] showed much higher modulus and strength, but the ductility was not improved until high content of comonomer, too. For an example, the elongation at break of poly(ethylene-co-1,4-cyclohexylene dimethylene 2,5-furandicarboxylate) (PECF) can be raised from 5% of PEF to 186% at 59 mol% CF unit, but only to 50% at 32 mol% CF unit [21]. Wang et al. [26] synthesized P(EF-mb-PEG) multiblock copolymers containing poly (ethylene glycol) (PEG) soft segments. The strength decreased to 27 MPa at 20 w% PEG content, but the elongation at break was slightly raised to 35% up to 60 w% PEG. The improvement of PEF ductility seems to be limited. For improving impact toughness of PEF, Park et al. [20] reported the first and sole result to date. They found the impact strength of PECF can be slightly improved with respect to PEF, from 3.1 kg cm/cm of PEF to 4.0 kg cm/cm of $PE_{25}C_{75}F$. Clearly, the improvement is also very limited.

In order to improve ductility and impact toughness of PEF and obtain PEF-based materials with balanced mechanical performance, in this study, PEF-based multiblock copolymers, namely, poly(ethylene 2,5-furandicarboxylate-mb-poly(tetramethylene glycol) (P(EF-mb-PTMG), or PETF for simplicity) were synthesized via melt polycondensation of dimethyl 2,5-furandicarboxylate (DMFD) and ethylene glycol (EG) in presence of PTMG diols. Chain structure and composition of the products were characterized with FTIR and ^{1}H NMR, and crystallization, fracture morphology and thermo-mechanical properties were assessed with DSC, XRD, TGA, SEM, tensile and notched Izod impact testing. The effect of chain length and content of PTMG on the structure and properties have been discussed. It is worth pointing out that PTMG is potentially biobased as well and has been employed as a precursor in synthesizing other poly(ether-ester) segmented copolymers including P(BT-mb-PTMG)s as the well-known commercial polyester elastomers [38,39] and P(BF-mb-PTMG)s as modified PBF materials [40]. However, to our best knowledge, synthesis and properties of P(EF-mb-PTMG)s have not been reported yet.

2. Experimental part

2.1. Materials

Dimethyl 2,5-furandicarboxylate (DMFD, 99.3% according to the supplier) was a product from Mianyang ChemTarget. Co. Ltd, China. Ethylene glycol (EG, 99%, Sigma), poly(tetramethylene glycol) (PTMG, $M_n \approx$ 1000, 2000 g/mol, Macklin) and Irganox 1010 (BASF) were used without any further purification. Home-made titanium-silica complex (Ti@Si, Ti 1 w% or 0.21 mmol Ti/g) was used as the catalyst for polymer synthesis. Phenol, 1,1,2,2-tetrachloroethane (TCE), acetone, ethanol, deuterated chloroform ($CDCl_3$) and deuterated trifluoroacetic acid (TFA-d_1) were all purchased from Sinopharm and used as received.

2.2. Synthesis of PEF and P(EF-mb-PTMG) (or PETF) copolymers

The PEF and P(EF-mb-PTMG) copolymers were synthesized from DMFD, EG, and PTMG via a two-stage melt polycondensation method (Scheme 1). The molar ratio EG/DMFD was fixed at 2, but the PTMG/EG mass ratio changed and ranged from 0 to 3.43. In the first step, the calculated amounts of DMFD, EG, PTMG, thermal stabilizer (Irganox 1010, 0.25 w% based on the total monomer mass), and catalyst (0.1 w % based on DMFD) were charged into a 250 mL four-necked round-bottom reactor equipped with a mechanical stirrer, N_2 inlet and reflux condenser. Then, the transesterification reaction was carried out at 170–200 °C for about 4 h under the protection of N_2 until there was no methanol, the byproduct, to be distilled out. In the second step, the reaction temperature was increased to 230–240 °C for polycondonsation reaction under a reduced pressure of about 100 Pa. The reaction was stopped when a so-called Weissenberg effect emerged. Finally, the products ware dried at 60 °C in vacuum for characterization.

For simplicity, the resulting multiblock copolymers, P(EF-mb-PTMG)s, are named as PETF, or more precisely, PET^{x}F-y, where x indicates the number-average molecular weight of PTMG (1K and 2K represent 1000 g/mol and 2000 g/mol, respectively) and y indicates the expected mass percentage of PTMG (φ_{PTMG}) to be fully incorporated into the copolymers, which is calculated according to equation (1). In the equation, m_{PTMG} and m_{DMFD} are the mass of PTMG and DMFD in