



# Synthesis and structure – property relationship of biobased poly(butylene 2,5-furanoate) – *block* – (dimerized fatty acid) copolymers



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## ABSTRACT

A series of poly(butylene 2,5-furanoate) – *block* – (dimerized fatty acid) (PBF-*b*-FAD) copolymers were successfully synthesized from 2,5-furandicarboxylic acid (FDCA), 1,4-butanediol (1,4-BD), and dimerized fatty acid diol (FADD) via a polycondensation in melt under the relatively mild process conditions and a reasonable excess of diol. The copolymers with different PBF to FAD segment ratio were characterized in regard of their chemical composition, microstructure, thermal transitions and stability as well as the mechanical performance. Some results were also discussed in relation to terephthalic acid based PBT-*b*-FAD copolymers, synthesized under the same experimental procedure. A detailed analysis of PBF homopolymer confirmed its relatively high molecular weight, semicrystalline structure, and in consequence a very good mechanical performance. In turn an incorporation of FADD amorphous segments between PBF blocks resulted in multiblocked structure with the ester group links and the real composition very close to those calculated theoretically. Although the specific furan ring architecture disturbs the macromolecules symmetry, thus the crystallization process, the PBF-*b*-FAD copolymers, varying in between 20 and 80 wt% of the rigid segments, reveal the heterogeneous microstructure. And the phase separation may be enhanced by the annealing above  $T_{cc}$ . In consequence the furan-aromatic copolyesters combine a variety of physical properties (also the elastomeric behavior), tunable by both PBF to FAD ratio and the thermal treatment, with a good processability. They are also characterized by almost twice higher level of the tensile stress and E modulus when compared to previously reported PTF-*b*-FADD copolymers. Considering the soon commercialization of bio-1,4-butanediol the presented materials have also a potential to be synthesized as fully bio-based.

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## 1. Introduction

The research activity aiming to replace the terephthalic acid (TPA) with the plant-derived 2,5-furandicarboxylic acid (FDCA) is recently gaining an importance. It is reflected by a quantity of published papers, and a multiplicity of approaches to the application of FDCA in the polymer synthesis with various monomers [1–4]. Particularly high interest is focused on the development of the synthesis paths of bio-based semicrystalline polyesters and

their copolymers due to their widespread usability as engineering, packaging, fiber forming and elastomeric materials [5,6]. Currently the commercial application of FDCA for the polymer production is still slowed down due to the insufficient availability on the monomer market stock. However the world's leading chemical companies announce highly advanced research in order to supply the market with the furan-aromatic polyesters competitive to TPA-based analogues. The press releases of Avantium, the European precursor in plant-derived FDCA technology development, report about the collaboration with the Japanese' Toyobo in optimizing the production of poly(ethylene furanoate) (PEF) resin at a commercial scale as well as the PEF thin films for the packaging purposes [7]. On the other hand DuPont™ together with Archer Daniels Midland

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Company are focused on developing the production of poly(trimethylene furanoate) (PTF), based on fructose-derived furan dicarboxylic methyl ester [8]. In both cases the low molecular mass diols used may also be obtained from the lignocellulosic feedstock bio-refinery [9], which makes the polyesters potentially 100% bio-based. Moreover, the furan polyesters, similarly to their petroleum counterparts, prove to be suitable as a rigid segment in ester multiblock copolymers [10,11].

Poly(butylene 2,5-furanoate) (PBF) is, besides PEF, the best described furan-based polyester [12–17]. It is due to a structural similarity to benzene-aromatic poly(butylene terephthalate) (PBT). This semicrystalline engineering thermoplastic is characterized by a high strength and rigidity, supreme thermal and chemical stability, electrical insulation properties, moisture, oxygen and aroma barrier as well as a short-cycle processing due to a fast crystallization rate [18]. Moreover the thermoplastic elastomers containing PBT as the rigid segment, combining the thermal processability with the elasticity of rubber, constitute the materials of the technological relevance [19,20]. In the near future PBF has also a chance to become the commercially available fully bio-based polyester due to starting-up the production of bio-1,4-butanediol (1,4-BD) on a commercial scale. The process is based on the direct conversion of the lignocellulose-derived sugar, i.e. dextrose, employing *E. coli* bacteria [21,22]. 1,4-BD from the renewable feedstock is already offered to the customers by BASF. The same company announced the formation of a joint venture with Avantium in order to improve the FDCA production capacity [23].

In our previous studies we reported on the synthesis and characterization of poly(trimethylene 2,5-furandicarboxylate) multiblock copolymers in which a dimerized fatty acid diol was applied as the flexible segment, and all reagents were biomass derived [24]. Considering the progress in the bio-monomers commercialization the currently presented materials, consisting of PBF rigid segments and dimerized fatty acid ester' (FAD) flexible segments, have also a perspective to extend the range of fully bio-based materials. The PBF-*b*-FAD copolymers containing different rigid to flexible segments' ratio were obtained via the polycondensation in melt in a two-step procedure. The idea of combining the TPA-based ester segments having 1,4-BD in a repeating unit and the dimerized fatty acid is not new, as there are a few papers from 90's describing the copolymerization of such materials in melt [25–27] or more recently the PBT modification in solid state [28,29]. However they have not been commercially applied. The idea of this paper is provide the comprehensive characteristic of novel multiblock copolymers revealing the features of thermoplastic elastomers. But also to understand the effect of the aromatic ring architecture on the copolymers performance. The PBF-*b*-FAD copolymers were examined in regard to their macromolecular and crystalline structure, phase transition temperatures, thermal stability and mechanical properties. The effect of the annealing process on copolymers' microstructure and performance is also analyzed. Some results are discussed in relation to TPA-based PBT-*b*-FAD copolymers, synthesized under the same procedure and having the same rigid to flexible segment ratio.

## 2. Materials and methods

### 2.1. Materials

2,5 – Furandicarboxylic acid (FDCA), 99%, was purchased from Matrix Fine Chemicals (Switzerland). The fatty acid dimer diol (FADD), named Pripol 2033 ( $M_w = 570$  g/mol), was kindly supplied by Croda (The Netherlands). It is the product of dimerization of C18 vegetable unsaturated linoleic acid. 1,4 – butanediol (1,4-BD) (Sigma Aldrich), tetrabutyl orthotitanate,  $Ti(OBu)_4$ , (Fluka) used as the catalyst, Irganox 1010 (Ciba – Geigy, Switzerland) applied as antioxidant, and sodium phosphate,  $Na_3PO_4$  (Sigma Aldrich) were reagent grade. Purified terephthalic acid (TPA), industrial grade, for PBT based copolymer' synthesis was kindly supplied by PKN Orlen (Poland).

### 2.2. Synthesis of the materials

Both FDCA – and TPA – based homopolymers and copolymers were synthesized via a two-stage melt polycondensation method using a 1 dm<sup>3</sup> capacious steel reactor [10] under different process parameters. In general the reactor was first pre-heated to 160 °C, then an appropriate amount of carboxylic acid with Irganox1010 (0.5 wt% in relation to the copolymer final mass) was charged, the reactor was sealed, and air was pumped out for ca. 20 min 1,4-BD in a molar ratio of diol to diacid 2:1 with one part of  $Ti(OBu)_4$  (0.25% in relation to diacid in total) was next poured under the nitrogen flow and a direct esterification of FDCA or TPA by 1,4-BD proceeded under a relevant temperature range (Table 1). During this step the released by-products (water and THF) were periodically distilled out. When the amount of the distilled by-product achieved 80% of theoretical value of water, the second part of the catalyst was added. In the case of the copolymer synthesis a relevant amount of FADD (0.2, 0.35, 0.5, 0.65 wt% in relation to PBF segment length) was also charged. The second stage – the melt polycondensation, was carried out in a specified temperature range under a reduced pressure of 25–30 Pa. During this time the excess 1,4-BD was distilled out from the reactor, and condensed in a glass flask. Progress in polymerization was monitored via an increase of the stirrer torque due to an increasing viscosity of the reactive mixture. The synthesis was carried out up to reaching the same value of torque for all materials. Finally, the polymer melt was extruded from the reactor under the nitrogen pressure, cooled to a room temperature in a water bath and then granulated.

The PBF and PBT homopolymers as well as the copolymers containing 35, 50, 65, and 80 wt% of the rigid segments have been prepared and subjected to the characterization. The PBF rigid segment content has been theoretically calculated based on the conventional flexible segments definition, which includes one furan acid unit within each FAD sequence (Fig. 1). The flexible segment is in fact the ester of dimerized fatty acid, and in the text the samples are denoted as PBF/FAD or PBT/FAD with a relevant number referring to the rigid segment wt % content. As the molecular mass of FADD was constant, the changes in copolymers' composition were controlled via changes in the PBF or PBT segment length.

**Table 1**  
The synthesis parameters of polyesters and copolymers depending of the diacid used.

Material	Diacid	Stage 1 Temp. range (°C)	Duration (min)	Stage 2 Temp. range (°C)	Duration (min)
PBF or PBF/FAD	FDCA	160–175	180	210–220	60
PBT or PBT/FAD	TPA	195–225	150	250–260	30

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