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Poly(ethylene furanoate-*co*-ethylene terephthalate) biobased copolymers: Synthesis, thermal properties and cocrystallization behavior

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ABSTRACT

A series of poly(ethylene furanoate-*co*-terephthalate) (PEFT) copolymers, with compositions ranging from neat poly(ethylene furanoate) (PEF) to poly(ethylene terephthalate) (PET), was synthesized by melt and solid state polycondensation (SSP). ^{1}H NMR spectra revealed that the copolymers were random, while the WAXD patterns of the copolyesters indicated isodimorphic cocrystallization. A minimum was observed in the plot of the melting temperature (T_m) vs composition while the glass transition temperatures (T_g) varied almost linearly with increasing ET units. The crystallization rates and degree of crystallinity decreased with comonomer content. Several thermodynamic models were applied for the analysis of the melting point depression. A small portion of the comonomer units was found to be introduced into the homopolymer crystals. It was also realized that it is easier to incorporate the EF units into the PET crystal than the opposite. PLM was used to observe the spherulitic morphologies formed during isothermal melt crystallization. Thermogravimetric analysis (TGA) indicated that the thermal stability of PEFTs decreases slightly with increasing furanoate content. Finally, the mechanism of decomposition was evaluated via Py-GC/MS, which consisted of mostly heterolytic scission and less of homolytic scission reactions.

1. Introduction

Poly(ethylene terephthalate) (PET) is one of the most important and highly produced man-made polymers [1]. It is synthesized from ethylene glycol (EG) and terephthalic acid (PTA) and the two monomers are both fossil based, currently. However, a novel process has been developed recently for the production of EG, involving direct conversion of lignocellulose to EG [2,3]. Furthermore, *p*-xylene, the precursor of terephthalic acid, has been obtained by catalytic conversion of platform chemicals or raw biomass. So, the synthesis of green PET from renewable resources seems feasible [4–8].

PET has been the most important polymer for beverage packaging over the past four decades. This comes as the result of its

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favorable properties such as its optical clarity, barrier properties, and competitive performance-to-cost ratio. Despite the fact that PET has met many of the current global packaging needs, there are still some drawbacks. For example it is characterized by high oxygen transmission rates which limit its effectiveness for oxygen-sensitive beverages. More importantly, one of its monomers, terephthalic acid (TA), is fossil based. Coca-Cola Co., in 2009 began to produce PET bottles based on 30% plant-based renewable material; monoethylene glycol made from sugarcane ethanol. In fact, the first fully-biobased PET bottle was exhibited by the company, at the 2015 World Expo in Milan [9]. Coca-Cola currently holds collaborations with Virent, Gevo and Avantium for the production of the bio-based PTA component (or PEF) for PlantBottle® [10]. The new 100% biobased PET bottle is based on technology developed by biofuels and from the biochemical company Virent, Inc., which enables production of BioFormPX (paraxylene) from beet sugars instead of fossil fuels [9].

Copolymerization and reactive blending of polyesters are often used for adjusting properties through the composition and constitution of the copolyesters. Chemical modification of PET by incorporating various glycol or acid comonomers has been intensively investigated in the past with the aim of extending the use of PET in new applications [11–19].

Interest in polymers from renewable resources has been growing as part of the general concern for sustainability [20–22]. Biomass is abundant, cheap and one of the most attractive alternative feedstocks in nature. So, it might be considered as a suitable replacement of fossil resources, used to produce high value-added chemicals and fuels. 2,5-Furandicarboxylic acid (FDCA) is one of the most promising chemicals, readily obtained by oxidation of 5-hydroxymethylfurfural (HMF) which in turn can be formed from polysaccharides and sugars [23–26]. In fact, technology pathways to biobased TPA are still under development, while FDCA is readily produced from renewable resources. While the structure of FDCA is similar to terephthalic acid (TA), differences exist in their ring size, polarity, and linearity, finally resulting in significantly different physicochemical properties. The interatomic distance between carboxylic acid groups is 5.731 Å in TA, while it is only 4.830 Å in FDCA. Moreover, the linear *p*-phenyl connection in TA results in an angle of 180° between carboxylic acid carbons, while FDCA shows a nonlinear structure which yields an angle of 129.4° [27].

FDCA recently gained much interest in polycondensates. It was found to be a possible substitute of terephthalic acid in aromatic polyesters such as PET, PBT or PTT. Poly(ethylene 2,5-furandicarboxylate) or poly(ethylene furanoate) (PEF) is entirely based on renewable resources, as it is produced from FDCA and ethylene glycol. PEF is new polymer with high performance properties, including barrier, thermal, and mechanical among others. A surprisingly large 19-fold carbon dioxide permeability reduction was found for PEF compared to PET [27]. A drastic reduction in oxygen permeability by a factor of about 11 × for PEF compared to PET has also been stated [28]. PEF and similar furanic polymers have been the subject of recent research, due to their renewable nature and promising properties [29–34]. PEF is expected to be a viable candidate for the polyester and food packaging market in the future [35–38].

Recently, a few studies on PEF-based copolymers have been published but as expected, their number is limited compared to those on PET related copolymers [22,38–45]. The cocrystallization in random copolyesters has been discussed in the past [46–50]. There is some evidence that the copolymer crystal includes different kinds of comonomer units in a crystalline lattice, which is an isomorphic phenomenon [51]. In such a case the minor component of crystal should influence the properties of solid copolymers. In fact cocrystallization is easier in aliphatic than in aromatic copolyesters [52–57]. Cocrystallization in copolymers based on ethylene terephthalate is of special interest and such copolymers are often used as model materials [57–61].

In this work, a full series of eleven PEFT copolymers, with compositions ranging from neat PEF to neat PET, were synthesized and the thermal and solid state properties were studied in detail. The cocrystallization behavior of the two comonomers was investigated, since this can be crucial for the overall performance of the copolymers and their potential applications as packaging materials.

2. Experimental

2.1. Materials

2,5-Furan dicarboxylic acid (2,5-FDCA, purum 97%), dimethyl terephthalate (purum 99%), ethylene glycol (EG) and tetrabutyl titanate (TBT) catalyst of analytical grade were purchased from Aldrich Co. 2,5-dimethylfuran-dicarboxylate (DMFD) was synthesized from 2,5-FDCA and methanol as described in our previous work [36]. All other materials and solvents used were of analytical grade.

2.2. Copolymer synthesis

Neat PEF and PET polyesters were prepared by the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor as described in previous works [36,62]. Bis(hydroxyl ethyl-furanoate) (BHEF) was synthesized by transesterification from DMFD and EG in a molar ratio of diester/diol = 1/2.2. Both reagents were charged into the reaction tube of the polyesterification apparatus with 400 ppm of TBT. The reaction mixture was heated at 150 °C under argon flow for 2 h, at 160 °C for additional 2 h and finally at 170 °C for 1 h. CH_3OH byproduct was removed from the reaction mixture by distillation and at the end of this step temperature was increased at 200 °C and vacuum was applied for 20 min in order to remove the EG excess, producing BHEF. Bis(hydroxyl ethyl-terephthalate) (BHET) was synthesized from DMT and EG using a similar procedure as described previously for BHEF production. The PEFT copolymers were then synthesized by melt polycondensation using different BHEF/BHET feeding ratios (Table 1). The mixture was heated at 220 °C for 2 h at stirring speed 720 rpm and vacuum application, at 230 °C for 2 h and at 240 °C for additional 1 h. Time was remained stable in all copolymers while used temperatures were gradually increased by 5 °C increasing BHET amount by 15%. After the polycondensation reaction was completed, the polyesters were easily removed, milled and