



Isothermal crystallization and structural characterization of poly(ethylene-2,5-furanoate)



G. Stoclet ^{a,*}, G. Gobius du Sart ^b, B. Yeniad ^b, S. de Vos ^b, J.M. Lefebvre ^a

^a Unité Matériaux et Transformations, UMR CNRS 8207, Université Lille1, Bat. C6, 59655 Villeneuve d'Ascq, France

^b Corbion Purac BV, Arkelsedijk 46, 4206 AC Gorinchem, The Netherlands

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ABSTRACT

Among “green” alternatives for oil-based commodity plastics like Polyethylene, Polyamides, and Poly(-Ethylene Terephthalate), a new class of polyesters synthesized from furandicarboxylic acids (FDCA) currently is in the spotlight of both the academic and industrial communities. Of particular interest is Poly(Ethylene-2,5-Furanoate) (PEF), which can be synthesized from monomers derived from sugars and exhibits physical properties that imply large substitution potential for PET in bottle, fiber and packaging applications. In this study the structure-thermal properties relationship of PEF have been investigated in order to explain the complex behavior exhibited by PEF during isothermal crystallization. Secondary crystallization and melt-recrystallization processes have been identified in order to explain the observed behavior. The existence of a critical crystallization temperature around 170 °C marking a transition in terms of crystalline phase induced is also pointed out. Moreover, data such as the molecular weight between entanglements (M_e) and standard melting enthalpy (ΔH_m°) have been determined. In addition the crystalline morphology was characterized by means of SAXS and WAXS. The influence of the crystallization conditions on this morphology is given. As a main result it has been found that depending on the crystallization temperature (T_c), a disordered or an ordered crystalline phase (called α' and α respectively) are formed at low ($T_c \leq 170$ °C) and high ($T_c \geq 170$ °C) temperatures, respectively. Finally, evidence for the formation of a rigid amorphous phase during crystallization is presented, indicating that a three-phase model has to be considered in order to provide an appropriate description of the morphology in semi-crystalline PEF.

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1. Introduction

Over the last decades considerable research efforts have been paid to find alternatives to petroleum-based polymers. Among these established polymers, Poly(ethylene terephthalate) (PET) is the dominant one for beverage packaging due to its appropriate physical properties such as thermal, mechanical, optical and barrier properties. A closely related family of 2,5-furandicarboxylic acid (FDCA)-based polyesters, such as Poly(Ethylene-2,5-Furanoate) (PEF) and Poly(butylene-2,5-furan-dicarboxylate [1] (PBF), have received much attention. Notably, PEF has been the topic of many studies, on the one hand because of its comparable thermal, yet improved barrier properties when compared to PET and PBT [2,3] and on the other hand owing to its better processing economics, greenhouse gas balance and carbon footprint [4]. PEF is a linear

aromatic polyester exhibiting a chemical structure similar to that of PET and has been known for more than 70 years. Eerhart et al. have shown that PEF production would reduce the non-renewable energy use by 40%–50% and the Greenhouse gas emissions by 45%–55%, as compared to PET. Synthesis of PEF at lab-scale has been studied by various researchers [2,5–8], while industrial approaches to synthesize high molecular weight PEF have also been proposed [6,10,11]. The diacid monomer in PEF, furan-2,5-dicarboxylic acid or FDCA, can be obtained via different routes from C6 sugars, while biobased mono-ethylene glycol or MEG is already established on a large scale. For example, Thiagarajan et al. recently reported the use of different isomers of FDCA, obtained from agro-residues, in polyester synthesis [9]. Furthermore the authors synthesized new copolyesters based on 2,4-FDCA and 3,4-FDCA isomers and (linear) diols. The characterization and comparison with their as-synthesized 2,5-FDCA analogs showed that using the 2,4-FDCA diacid yields a fully amorphous PEF exhibiting similar glass transition and a higher degradation temperature.

* Corresponding author.

E-mail address: gregory.stoclet@univ-lille1.fr (G. Stoclet).

Regarding physical properties of PEF only few studies have been carried out, most of them being focused on the characterization of the thermal behavior. Both de Jong et al. and Knoop et al. reported on the melt- and solid-state polycondensation and the thermo-mechanical characteristics of PEF and other FDCA-copolyesters. Knoop [10] showed that PEF exhibits a similar Young's modulus as PET, but displayed brittle fracture. The increase of PEF crystallinity by annealing above its T_g resulted in a higher stiffness of the notably nonoriented material. They also reported the occurrence of multiple melting behavior during heating of semi-crystalline PEF which they attribute to a melting recrystallization process. The same observations and interpretations were reported by van Berkel et al. [11].

In a more recent paper, Papageorgiou et al. report a comparison of the thermal behavior of PEF with PET and Poly(ethylene naphthalate) (PEN) [12]. In summary, they confirmed data reported by Gandini in 2008 that the glass transition (T_g) of PEF is slightly higher than the one of PET but lower than the one of PEN and that the melting temperature of PEF is lower by 30 °C and 50 °C than the ones of PET and PEN, respectively. In their study the authors also reported the existence of multiple melting endotherms during heating of semi-crystalline PEF. They attribute the presence of these multiple endotherms to i) melting of secondary crystals and ii) the presence of two populations of lamellae of different stability rather than a recrystallization process. Still regarding thermal properties, authors determined the standard melting enthalpy of PEF equal to $\Delta H_m^\circ = 137$ J/g, that is to say quite similar to the ΔH_m° value for PET equal to 140 J/g [13]. They also determined the equilibrium melting enthalpy of PEF to be equal to 265 °C. Finally, they report that PEF has slower crystallization kinetics than PET, which is in agreement with earlier findings of de Jong et al. In opposition a value of $\Delta H_m^\circ = 185$ J/g determined via density measurements has been proposed by van Berkel et al. [12].

A recent study of Codou et al. focused on the non-isothermal crystallization kinetics of PEF synthesized from a direct esterification process [14]. By comparing the crystallization kinetics for cold crystallization and melt crystallization, they found that even if crystals show similar structures, different crystal growth dynamics are observed. Particularly a faster crystallization rate was observed when PEF was cold crystallized by heating from the glassy state.

While few studies dealing with the characterization of the thermo-mechanical behavior of PEF were published, as the polymer has limited availability, reports on the structural characteristics of this polyester are even more scarce. Regarding the crystallography of PEF, only an early work by Kazaryan et al. reports a triclinic unit cell for PEF [15]. Diffraction patterns of semi-crystalline PEF have been also reported by several authors [3,11,13,15]. To our knowledge only one type of diffraction pattern has been reported for PEF up to now meaning that only one crystalline phase has been actually encountered. In their comparison of PEF with PET and PEN, Papageorgiou et al. observed some similarities of the WAXS patterns between PET and PEF, which seems to indicate that both polymers exhibit similar crystalline structures [13]. The same observations were reported by Burgess et al. regarding the comparison of PEF and PET [3]. In their work, these authors also demonstrate by studying the sub-ambient viscoelastic relaxations that PEF exhibits slower chain mobility than PET due to a more rigid monomeric unit. Finally they also report a higher amorphous phase density for PEF to explain its higher oxygen barrier properties.

Knowledge of the structure-property relationship of a polymer is of prime interest in the framework of the optimization of its end-use properties. According to this goal, the present study is aimed at elucidating the relations between crystallization behavior and the associated structural evolution of PEF. The influence of crystallization conditions on the morphology of PEF was assessed, and the

encountered complex melting behavior was investigated using wide- and small angle X-ray scattering techniques in order to monitor the structure of PEF at different length scales.

2. Experimental

2.1. Material

The PEF resin was supplied from Corbion Purac BV. PEF was prepared from direct esterification of Corbion polymer-grade 2,5-FDCA and bio-based mono-ethylene glycol (MEG) as supplied commercially by India Glycols, followed by polycondensation using antimony trioxide as the catalyst. The resin was reactor-grade and was not subjected to solid-state post-condensation. Before processing, the PEF pellets were dried under vacuum at 80 °C for 12 h in order to remove any residual moisture. 200 μ m thick sheets were obtained by compression molding at 250 °C during 5 min under a pressure of 50 bars followed by a rapid cooling. 1 mm thick samples were also obtained using the same protocol for the viscoelastic property measurements.

2.2. Molecular weight determination

Molecular weights (M_n , M_w , M_z) and polydispersity (M_w/M_n) were determined by Size Exclusion Chromatography (SEC) performed on a Malvern Viscotek TDAMax VE2001, equipped with a light scattering detector, viscosity and concentration detectors. Samples were filtered over a 0.45 μ m PVDF filter. The eluent was hexafluoroisopropanol (HFIP) + 0.02 M CF_3COOK at a flow rate of 0.70 mL/min running at 40 °C over two PSS PFG analytical linear M columns. The absolute molecular weights were calculated using multi detectors calibration and a narrow PolyCAL™Std-PMMA-65K standard (Malvern).

2.3. Thermal behavior

Thermal properties and crystallization kinetics were evaluated by means of Differential Scanning Calorimetry (DSC) experiments. A Diamond DSC (Perkin Elmer) apparatus was used. For each heating rate used in this study, temperature and heat flow were calibrated with a high purity indium sample using standard procedures. For the specific experiments dealing with the quantification of the mobile amorphous phase, calibration was performed with a sapphire using the associated specific procedure. Experiments were carried out under nitrogen flow on about 10 mg samples placed in aluminum pans. Temperature scans were performed between 25 °C and 250 °C at heating and cooling rates in the range 2 °C/min to 50 °C/min. The crystallization behaviors from the molten and solid states at different crystallization temperatures (T_c) were analyzed. The thermal programs used for this purpose are depicted in Fig. 1.

In each case the sample was held at 250 °C for 3 min in order to erase the thermal history of the material. Samples were subsequently:

- Quenched directly to T_c and maintained at this temperature during the crystallization time t_c for melt crystallization.
- Quenched to 25 °C and then heated at 50 °C/min to T_c and maintained at this temperature during the crystallization time t_c for solid state crystallization.

Finally, samples were quenched to 25 °C before being analyzed at a heating rate of 10 °C/min. Crystallization temperatures were varied from 140 °C to 190 °C.

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