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Crystalline and supermolecular structure evolution of poly(ethylene terephthalate) during isothermal crystallization and annealing treatment by means of wide and small angle X-ray investigations

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ABSTRACT

Small-angle X-ray scattering, wide-angle X-ray diffraction and differential scanning calorimetry analysis were carried out to evaluate the evolution of the supermolecular structure of poly(ethylene terephthalate) (PET) during isothermal crystallization and annealing process. PET was crystallized from the melt by isothermal treatments at 226 °C. Partially crystallized samples were prepared interrupting the crystallization by quenching, while prolonged treatments were performed to prepare annealed samples. The adopted crystallization procedures allowed to form crystals which developed during primary and secondary crystallization, and the annealing process. On the basis of X-ray data, the lamellar and amorphous phases were unambiguously attributed. The lamellar thickness and the crystallinity progressively enhance with increasing the time of thermal treatment; on the contrary, the long period decreases and this effect is mainly due to the contraction of the amorphous phase. The melting behaviour of the annealed samples indicates that the heating-induced crystal reorganization phenomena are inconsistent. The interdependency between the melting temperature and the crystal thickness allowed to extrapolate the equilibrium melting temperature.

1. Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic engineering polymer of high industrial and commercial interest. Considerable efforts have been made to understand its structure organization and thermal behaviour. Small-angle X-ray scattering (SAXS) technique was largely used to calculate the periodicity and the thickness of constituent phases in the one-dimensional model for semicrystalline PET. The decrease of the periodicity was undoubtedly observed with increasing the isothermal crystallization time, while the ambiguity in the attribution of the phases to the amorphous and crystal thickness was source of large debate [1–7]. The uncertain in the assignment of SAXS data caused conflicting interpretation of the multiple melting behaviour of crystalline PET. Two different structural models were generally proposed to account for the dimensional and thermal data [8–13]. The first model proposes the presence of multiple lamellar population. In this approach lamellar stacks are separated by large gaps of amorphous material even after complete crystallization. The presence of lamellae with different thickness is generally proposed in two different variants of the model: separated stacks constituted of thin and thick lamellae and, alternatively, stacks constituted of thin lamellae inserted between thicker lamellae in the same stack. The second model is based on space-filling lamellar stacks homogeneously distributed. This model provides for a monomodal distribution of lamellar thickness and agrees to the melting–recrystallization–remelting interpretation of multiple melting endotherms.

We intend to contribute the topical discussion about the evolution of the PET supermolecular structure during

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the isothermal crystallization from the melt and the annealing process. In this paper, we present a detailed investigation of PET crystalline structure carried out by X-ray and differential scanning calorimetry (DSC) techniques. The adopted thermal procedures allow the preparation of samples partially crystallized during primary and secondary crystallization and annealed samples with different crystal perfection degree. To the best of our knowledge, for the first time the characterization of the crystalline and supermolecular structure of partially crystallized PET is carried out in thermodynamically stable conditions.

2. Experimental

2.1. Measurements

The wide-angle X-ray diffraction (WAXD) data were obtained at 25 °C using a Siemens D-500 diffractometer equipped with a Siemens FK 60-10 2000W tube (Cu K_α radiation, λ = 0.154 nm). The operating voltage and current were 40 kV and 40 mA, respectively. The data were collected from 5 to 40 $2\theta°$ at 0.02 $2\theta°$ intervals and the degree of crystallinity (X_c) was calculated by using the area integration method [14].

SAXS measurements were conducted at 25 °C with a Kratky Compact Camera. Monochromatized Cu K_α radiation (λ = 0.154 nm) was supplied by a stabilized Siemens Krystalloflex 710 generator and a Siemens FK 60-04, 1500W Cu target tube operated at 40 kV and 30 mA. The scattered intensity was counted in different ranges of $2\theta°$, by using a step scanning proportional counter with pulse height discrimination. For all the SAXS measurements the abscissa variable was $h = \sin(\theta)\ 4\pi/\lambda$. The experimental scattering data were analyzed considering the pseudo-two-phase model. The model consists of alternating parallel amorphous and crystalline lamellae connected by a transition layer, which can be represented as a linear variation of the electron density between the crystalline and amorphous cores. The data were desmeared and elaborated according to the approach proposed by Vonk and coworkers [15–19]. The correlation function was calculated as:

$$\gamma(r) = \int_0^\infty I_L(h)\cos(hr)dh/Q \quad (1)$$

where I_L is the Lorentz-corrected intensity and Q is the invariant, which is defined as:

$$Q = \int_0^\infty I_L(h)dh \quad (2)$$

The method allowed to calculate the relative two-phase fractions x_1 and x_2. About the two methods proposed by Vonk and Kortleve to calculate x_1, we adopted [15]:

$$x_1(1-x_1)L_n = A \quad (3)$$

where L_n is the position in the first maxima and A is the first intercept with the abscissa of the correlation function, respectively.

Thermal analysis was carried out by DSC using a Perkin-Elmer Pyris 1 system equipped with a liquid subambient device. The instrument was calibrated with indium standard. In a typical isothermal crystallization run, the polymer was heated up to 275 °C and held at this temperature for 5 min to cancel previous thermal history. Then, the sample was cooled at a nominal rate of 500 °C min^{-1} to the selected crystallization temperature of 226 °C. The heat flow evolved during the isothermal crystallization was recorded as a function of time. In measuring melting characteristics samples were heated at 20 °C min^{-1}.

2.2. Sample preparation

The PET sample used in this work was a commercial material produced by Shell (Caripack P82), with a M_n value of 28,000 g mol^{-1} and a polydispersity index equal to 2.1.

The thermal treatments adopted for preparing the PET samples were performed in the DSC instrument. In a typical preparation the polymer was maintained at 275 °C for 5 min, then was rapidly cooled to 226 °C. Partially crystallized samples P1, P2 and P3 were prepared interrupting the crystallization at different time periods by quenching in liquid nitrogen.

The weight fraction of the material crystallized at time t (X_t,) was calculated by the relation:

$$X_t = \int_0^t (dH/dt)dt \Big/ \int_0^\infty (dH/dt)dt \quad (4)$$

where the first integral represents the heat generated between the beginning of crystallization and time t, and the second represents the total heat generated at complete crystallization. In Fig. 1, the fraction of the crystallized material is reported as a function of the crystallization time, pointing out the partial crystallinity reached by the P-series samples. X_t is set equal to 1 when the isothermal crystallization is complete, i.e. the sample T1.

Finally, samples crystallized in the same condition adopted to prepare T1 sample were afterward annealed

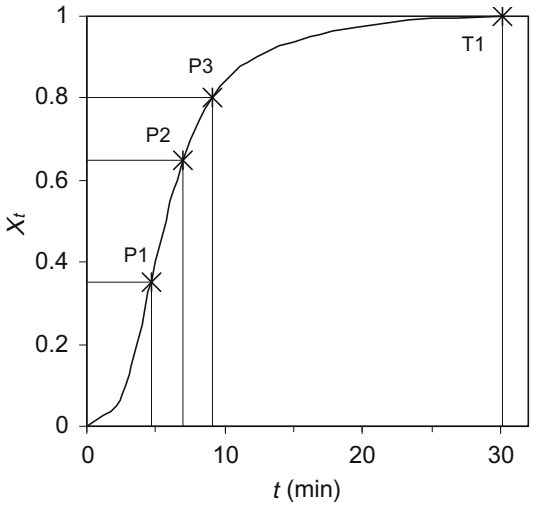

Fig. 1. Development of relative crystallinity (X_t) with time (t) for PET isothermal crystallization at 226 °C. The crystallization times adopted to prepare partial and complete crystallized samples are evidenced.