



Temperature dependence of the rigid amorphous fraction in poly(ethylene terephthalate)



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ABSTRACT

The analysis of the c_p melting curve of poly(ethylene terephthalate) (PET) after non-isothermal crystallization, according to a three-phase enthalpy-based procedure, has allowed to monitor the correct crystalline and rigid amorphous fractions evolution during fusion at low heating rate and to identify the temperature of complete mobilization of the rigid amorphous fraction, located in the proximity of 215 °C. This limit temperature for the disappearance of the rigid amorphous fraction in PET corresponds to the transition between the triple and the double melting behaviour displayed by PET after isothermal crystallization. The multiple melting behaviour of PET is usually attributed to the fusion of original crystals recrystallized during the heating at conventional scanning rate, and to the presence of dual lamellar stacks. In the present study, PET was isothermally crystallized at various temperatures (T_c) ranging from 185 °C to 225 °C, and the double and triple melting profile that is observed at conventional DSC heating rates, after isothermal crystallization at T_c higher and lower than 215 °C respectively, has been put in relation with the absence and the presence of RAF around the original crystal lamellae. All the experimental evidences here reported indicate that the critical temperature for the formation and the disappearance of the rigid amorphous fraction in the PET sample analyzed in the present study at conventional DSC scanning rates, is around 215 °C.

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1. Introduction

The common description of semicrystalline polymers as constituted by two separate phases, amorphous and crystalline, has been recently replaced by a more complete one that takes into account also the intermediate nanophase present at the interface between the crystalline and the surrounding amorphous regions [1]. The decoupling between crystalline and amorphous phases is in general incomplete, due to the length of the polymer molecules, which is much higher than the dimensions of

the crystalline phase, at least in one direction. The interphase between crystalline and amorphous regions is non-crystalline and includes amorphous chain portions whose mobility is hindered by the near crystalline structures. This interphase is generally named “rigid amorphous fraction” (RAF), its mobility being lower than that of the unconstrained amorphous phase, which is usually addressed as “mobile amorphous fraction” (MAF).

The temperature at which the rigid amorphous fraction vitrifies or mobilizes is often located between the glass transition (T_g) of the unstrained amorphous phase and the melting temperature, but this is not a general rule. In a few polymers the presence of RAF may cause a separate glass transition [1], but more often the exact location of

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the RAF vitrification and devitrification cannot be directly identified, because these processes are associated to the continuous and progressive change of the structure between liquid and solid and viceversa that occurs during cooling and heating. Due to the various degrees of coupling between the non-crystallized and crystallized chain portions, RAF vitrification and devitrification can take place in a very wide temperature range, often overlapping crystal ordering and disordering [2].

A detailed knowledge of the nanoscale phase behaviour of semi-crystalline polymers is decisive for the assessment of their mechanical, thermal, gas permeability and other macroscopic properties [3–8]. By acting as stress transfer point, the RAF produces an increase in the elastic modulus, with a behaviour similar to that of the crystal phase [3,4,7]. The rigid amorphous fraction affects also the barrier properties, due to its higher free volume with respect to the mobile amorphous region, which results in a different diffusion rate of small molecules [5–8].

The relationship between crystal growth and rigid amorphous fraction development, and between melting and rigid amorphous fraction mobilization has been detailed in the literature only for a limited number of semi-crystalline polymers [9–17]. These studies, performed independently of one another, in different crystallization and melting conditions and with different methods of data processing, if combined and compared with one another, prove that the different thermal histories affect the combined evolution and disappearance of crystalline and rigid amorphous phases.

During crystallization of poly(ethylene terephthalate) (PET) and poly[(R)-3-hydroxybutyrate] (PHB) at temperatures slightly above the respective T_g 's, vitrification of the rigid amorphous fraction parallels crystal growth [10,11], whereas in isotactic polystyrene (iPS) crystallized at 140 °C and 170 °C, i.e. well above the bulk T_g , the rigid amorphous fraction increases markedly after spherulite impingement, which corresponds to the beginning of the crystallization in restricted regions [14,15]. Upon slow cooling from the melt, both in iPS and PET, RAF vitrification takes place during the final stages of the non-isothermal crystallization process [12,16]. Conversely, a much slower cooling rate from the melt, attained with quasi-isothermal step cooling, results in vitrification of the RAF in PET and poly(trimethylene terephthalate) mainly after conclusion of the crystallization [13,17].

The influence of crystallization temperature was systematically investigated for poly(L-lactic acid) (PLLA) and PHB [18–20]. In order to verify the possible existence of a general rule for the development and the disappearance of the rigid amorphous fraction, the crystallization and melting processes of PLLA and PHB were studied and analyzed by conventional and temperature modulated DSC. Both in PLLA and PHB, the rigid amorphous fraction develops in parallel to the crystal phase at low crystallization temperatures, whereas at higher T_c the rigid amorphous fraction is established only during the final stages of crystallization, in correspondence with the growth of secondary crystals [18–20]. Investigation into the crystallization and melting behaviour of PLLA and PHB suggested the existence of a limit temperature for the formation and the dis-

appearance of the rigid amorphous fraction in the analyzed samples, which resulted approximately 130 °C and 70 °C respectively [18–20].

Also the melting process was found to be partially linked to RAF mobilization for a number of different semi-crystalline polymers [9,10,13–15,17–26]. For PHB, PET, iPS and *cis*-1,4-polybutadiene, the lower-temperature endotherm was probed to be connected with both partial fusion of the crystalline portions and enthalpy recovery subsequent to structural relaxation of the rigid amorphous fraction [14,15,19,21,22,26]. For PHB and bisphenol A polycarbonate, complete RAF mobilization was found to be achieved in correspondence with the lowest endotherm [9,10,19]. On the contrary for poly(1-butene) the RAF devitrification resulted completed well below the melting region [3,25].

In order to verify the possible existence of a general rule for the development and the disappearance of the rigid amorphous fraction in PET, the crystallization and melting processes were studied and analyzed by conventional and temperature modulated differential scanning calorimetry.

2. Experimental methods

Poly(ethylene terephthalate) (PET) of molar mass $M_w = 21,400 \text{ g mol}^{-1}$, was kindly received through the Bank of Crystallizable Polymers of European funded COST Action P12. After drying under vacuum at 100 °C for 16 h, the sample chips were compression-molded with a Carver Laboratory Press at a temperature of 280 °C for 3 min, without any applied pressure, to allow complete melting. After this period, a pressure of about 100 bar was applied for 2 min. Successively the sample was quickly cooled to room temperature by means of cold water circulating in the plates of the press. The thickness of the resulting film was about 200 μm .

Differential scanning calorimetry (DSC) and temperature-modulated calorimetry (TMDSC) measurements were performed with a Perkin Elmer Differential Scanning Calorimeter DSC 8500 equipped with an IntraCooler III as refrigerating system. The instrument was calibrated in temperature with high purity standards (indium, naphthalene, cyclohexane) according to the procedure for standard DSC [27]. Energy calibration was performed with indium. To gain precise heat capacity data from the heat flow rate measurements, each scan was accompanied by an empty pan run and calibration with sapphire [27].

Dry nitrogen was used as purge gas at a rate of 30 mL min^{-1} . A fresh sample was employed for each analysis to minimize thermal degradation. All results presented and discussed are the average of repeated runs. Before each analysis, the compression-molded PET samples were heated from room temperature to 280 °C at a rate of 50 $^\circ\text{C min}^{-1}$ and maintained at this temperature for 3 min, in order to completely destroy the previous crystal order.

After rapid cooling of the samples from 280 °C to 250 °C (needed to minimize thermal degradation of the polymer), non-isothermal crystallization of PET was followed both by TMDSC and conventional DSC down to 40 °C at

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