Contribution of chain alignment and crystallization in the evolution of cooperativity in drawn polymers

F. Hamonic [a], D. Prevosto [b],**, E. Dargent [a], A. Saiter [a],*

[a] AMME-LECAP EA4528 International Laboratory, Institut des Matériaux de Rouen, Université et INSA de Rouen, BP12, 76801 Saint Etienne du Rouvray Cedex, France
[b] Institute for Chemical and Physical Processes, CNR, Largo Pontecorvo 3, 56127 Pisa, Italy

ABSTRACT

The effects of Strain Induced Crystallization and chain orientation on the cooperativity evolution with temperature are studied on two polymers with similar molecular structure but different crystallization attitude. For this goal, we focus on poly(ethylene terephthalate) (PET) and the copolyester poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate) (PETg), the last one having very low ability to crystallize. From Temperature Modulated Differential Scanning Calorimetry and Broadband Dielectric Spectroscopy investigations, we show that the crystalline phase appearance in PET implies a large reduction of the Cooperative Rearranging Region size, accompanied with a variation from fragile to strong behavior of the structural relaxation time temperature dependence. Such large variations are not observed in PETg at the same draw ratio. In the case of PETg, a small contribution of chain alignment to the CRR size evolution is evidenced.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Understanding the influence that mechanical treatments have on polymer dynamics is of fundamental importance for a deeper comprehension of the polymer physics, in particular the relation of glass transition phenomenon to macromolecule organization. Mechanical treatments of polymers modify the macromolecule organization and their physical properties. As an example, drawing process can produce chain alignment in the draw direction and in some cases the appearance of a crystalline phase, this phenomenon being called Strain Induced Crystallization (SIC) [1–10]. Also, electrospinning technique used in the production of polymer nanofibers induces chain alignment along the fiber axis and in some polymers the growth of a crystalline phase [11–13].

Since the theory proposed by Adam and Gibbs [14], it is well accepted that the relaxation process related to the glass transition, called α relaxation process, is cooperative in nature: a structural unit can move only if a certain number of neighboring structural units also are moving. This concept implied the notion of Cooperative Rearranging Region (CRR), which can be estimated according to different models and theories in terms of structural unit number belonging to that, or in terms of characteristic length scale [15–24]. In the recent years, the evolution of CRR size upon varying external parameters as well molecular characteristics has been experimentally studied to understand how cooperativity correlates with other relaxation parameters such as fragility, glass transition temperature, relaxation time. However the influence of drawing on CRR has not deeply investigated.

According to Donth et al. [19], a CRR can be estimated from the von Laue approach describing a system with a fluctuating temperature. Each CRR represents a fluctuating region of molecular mobility (relaxation time) and it can be represented as a group of "sub-subsystems" called structural units, each one having its own glass transition temperature related to its own relaxation time. In a recent work [25] by assuming that temperature and polarization fluctuations have the same relaxation time distribution, we proposed to extend the Donth's approach initially based on calorimetric measurements to dielectric measurements. In such a way it is possible investigating the cooperativity evolution with temperature, from the crossover temperature to the glass transition temperature.

In semicrystalline polymers, the crystalline phase confines the amorphous one thus affecting the α relaxation dynamics. This effect depends on the crystallinity degree and on the crystal morphology

[26–28]. In the case of amorphous phase confinement due to the presence of crystalline lamellae induced by thermal crystallization, several studies show that the greater the crystallinity degree, the smaller the cooperativity length [29–34]. The originality of this work is the study of cooperativity evolution in the case of SIC, this crystallization mode inducing crystallite formation not spherulites. Furthermore, in order to consider not only the effects of crystallization but also of chain orientation, this work is focused on poly(-ethylene terephthalate) (PET) and the copolyester poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate), PETg. In fact, PETg is molecularly similar to PET in structure with the adjunct of a few percent of ethylene glycols and of cyclohexane-1,4-dimethanol, CHDM [35]. Such small modification is sufficient to avoid almost completely the crystallization in PETg. With respect to previous reports on the cooperativity evolution during crystallization, the most original contributions of this paper are distinguishing the effects of chain orientation and crystallization on the evolution of the cooperativity. Moreover, the study of cooperativity evolution from the Donth's approach over a broad temperature interval, from the glass transition up to the onset of cooperativity, is here proposed for the first time in the case of strain induced crystallization, this crystallization mode inducing crystallite formation not spherulites. By this way, we studied materials with a structural anisotropy, which is not the case in the majority of semicrystalline polymers studied in the literature.

2. Experiment

2.1. Materials

PET samples are obtained from 500 μm thick films extruded by Carolex Co. The number-average molecular weight is $\overline{M}n = 31{,}000$ g mol^{-1} and the density is equal to $\rho = 1.336$ g cm^{-3}. PETg plates ($4 \times 4 \times 0.2$ cm^3) are obtained from pellets by injection molding. The PETg used (6763 from Tennessee Eastman Co.) is an amorphous copolymer, consisting of cyclohexanedimethanol, ethylene glycol and terephthalic acid with a molar ratio of approximately 1:2:3. The number-average molecular weight is $\overline{M}n = 26{,}000$ g mol^{-1} and the density is equal to $\rho = 1.27$ g cm^{-3}. PET and PETg films are uniaxially drawn at a strain rate of 0.14 s^{-1} at 100 °C, the draw temperature being chosen just above the glass transition to avoid cold crystallization. After drawing, samples are cold air-quenched down to room temperature in order to prevent chain relaxation. The draw ratio ranges studied in this work are $1 \leq \lambda \leq 6.6$ for PET and $1 \leq \lambda \leq 7.6$ for PETg. For more clarity, the samples studied will be noted PETλ and PETgλ where λ indicates the draw ratio.

2.2. Temperature Modulated Differential Scanning Calorimetry

Temperature Modulated Differential Scanning Calorimetry (TMDSC) experiments have been performed in a Thermal Analysis instrument (TA DSC 2920) equipped with a low-temperature cell (minimal temperature = 203 K). Nitrogen was used as purge gas (70 mL/min). The TMDSC experiments have been performed in "Heat-Iso" mode (oscillation amplitude of 0.318 K, oscillation period of 60 s and heating rate of 2 K/min), which is advised for the study in semicrystalline polymers [36]. Calibration in temperature and energy was carried out using standard values of melting of indium and zinc. Calibration in specific heat capacity was carried out using sapphire as a reference. More details about calibration are given in reference [37].

From TMDSC, different signals can be obtained: the classical total heat flow and the apparent specific complex heat capacity C_p^* calculated as

$$\left| C_p^* \right| = \frac{A_q}{A_\beta} \times \frac{1}{m} \tag{1}$$

where A_q is the amplitude of the modulated heat flow, A_β the amplitude of the modulated heating rate and m the sample mass. Due to the phase lag φ between the calorimeter response function (i.e. the total heat flow) and heating modulation, two apparent heat capacity components noted C_p' (the in-phase component) and C_p'' (the out-of-phase component) are calculated according to the following equations:

$$C_p' = \left| C_p^* \right| \cos\varphi \tag{2}$$

$$C_p'' = \left| C_p^* \right| \sin\varphi \tag{3}$$

The C_p' versus temperature curve appears usually as an endothermic step at the glass transition temperature, and the C_p'' shows a peak in the glass transition region.

2.3. Dielectric spectroscopy

Dielectric relaxation spectra were measured with an Alpha Analyser from Novocontrol (measurement frequency interval: 10^{-2}–10^7 Hz), with a parallel plate capacitor cell, and the temperature was controlled through a heated flow of nitrogen gas, by means of a Quatro Cryosystem. Measurements have been performed in the temperature interval 320 K $< T <$ 433 K, with the exception of undrawn PET sample that has been measured up to 378 K because of appearance of thermal crystallization. Samples have been dried in vacuum at a temperature of about 343 K before measuring, and during the whole period of the measurement were kept in a pure nitrogen atmosphere.

3. Results

3.1. TMDSC data

Representative measurements of C_p'' are reported in Fig. 1 for undrawn samples (PET1.0 and PETg1.0) and for the maximal draw ratio (PET6.6 and PETg7.6). The curves corresponding to the classical endothermic step are published in another work [38]. For undrawn samples (black curves in Fig. 1), we observe a narrow peak with a maximum at the characteristic temperature T_α (Table 1). Due to the rather low frequency used, T_α from the reported TMDSC measurements is close to the glass transition temperature classically measured by DSC: $T_\alpha = 348$ K for PET1.0 and $T_\alpha = 349$ K for PETg1.0 (Table 1). For drawn samples (red curves (in web version) in Fig. 1), the behavior depends clearly on the sample studied: for PET6.6, we observe a broadening of the peak and a shift at high temperature ($T_\alpha = 380$ K). This shift of 30 K is very significant and can be correlated to the appearance of crystalline phase induced by drawing. Indeed, the crystallinity degree is equal to 37% for PET6.6 (see Table 1), producing a glass transition temperature increase due to the coupling effect [39,40]. This effect can be explained by the fact that the glass transition in the Mobile Amorphous Phase (MAP) is often crystallinity-dependent, and large variations of glass transition temperatures with the crystallinity degree could be observed for polyesters [41]. For PETg7.6, we also observe a broadening of the peak but less significant than for PET. As shown in Table 1, the crystallinity degree is equal to 5%, this low value explaining the absence of shift in the peak position.

According to Donth's approach mentioned in the introduction, the CRR average volume denoted as V_α can be estimated according to the following equation [19,42]: