



Rigid amorphous fraction versus oriented amorphous fraction in uniaxially drawn polyesters



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ABSTRACT

Structural changes in poly(ethylene terephthalate) PET and the copolyester poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate) PETg occurring during uniaxially drawing at 100 °C have been investigated as a function of draw ratio. This work compares the “microstructural” and the “thermodynamic” three phase description of drawn polyester films. Using Wide angle X-ray Scattering, both materials were characterized considering crystals, isotropic and oriented amorphous phases. Temperature Modulated Differential Scanning Calorimetry allows to evaluate the fraction of crystals, mobile and rigid amorphous fractions (MAP and RAF respectively). Above a critical draw ratio, RAF appears as soon as a strain induced crystalline (SIC) phase is developed for both materials. The degree of crystalline phase is lower and takes place at higher draw ratio for PETg than for PET. For PET, the oriented amorphous phase is composed by the RAF and a part of the MAP. For PETg, the SIC takes place in PET-rich regions and the quantity of RAF per crystal is high.

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1. Introduction

It has been recognized that semi-crystalline polymers cannot be described very well in terms of a simple two phase crystalline–amorphous model. Different kinds of phases have been proposed in literature [1]. Appearance of mesophases during the thermo-mechanical treatment of polymers was evidenced using Wide angle X-ray Scattering WAXS method for various polymers such as poly(ethylene terephthalate) (PET) [2] or poly(lactic acid) (PLA) [3]. The mesophase is an intermediate state between amorphous and crystalline phases; it possesses some degree of medium-range order. In a recent work [4], Cebe et al. demonstrate that combinations of thermal analysis and WAXS are the key techniques to characterize the phase structure of polyester fibers. They quantified for the first time the PLA mesophase in as-spun nanofibers. Wu et al.

[5] claimed that there are two types of non-crystalline domains in PET fibers: an isotropic amorphous phase and a highly oriented noncrystalline region. They estimated the amount of these two phases from two-dimensional WAXS patterns. Similarly, from X-ray diffraction of PET fibers, Wunderlich separated the non-crystalline scattering into an amorphous phase and an oriented intermediate phase [6,7]. In the case of Nylon-6 fibers, Murthy et al. have proposed a method for evaluating the isotropic and non-isotropic non crystalline phases from X-ray diffractograms [8].

Three phase model was also developed to describe the isotropic microstructure of thermally crystallized polymers. The incomplete decoupling due to tie molecules between crystalline and non-crystalline phases leads to a decrease for the amorphous phase chain mobility [9], and implies to describe most of the quiescent crystallized polymers with a three phase model: the crystalline phase, the mobile amorphous phase (MAP), and the rigid amorphous fraction (RAF) [1,10,11]. The RAF is the result of strong

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restrictions of amorphous chain segment mobility, due to the polymer chain part fixation to the crystalline lamellae [12]. Androsch and Wunderlich [13] showed, in various annealed PET, that the RAF amount must be considered as a measure of the coupling between the crystalline and the amorphous phase. Recently, it has been shown for Polytetrafluoroethylene (PTFE) that the mechanical relaxation temperature of the RAF is very different than those of the MAP and strongly dependent on the crystallinity degree [14]. The MAP glass transition phenomenon is also often crystallinity-dependent and large variations of glass transition temperatures with the crystallinity degree could be observed for PET [15,16]. As shown by Wunderlich [1], thermal analysis is a powerful tool to investigate the various nanophases in semi-crystalline polymers and allows for the calculation of the RAF, MAP and crystalline content in a semi-crystalline polymer. Knowledge of the microstructure of drawn semi-crystalline polymers is complex and some correlations have been attempted between the three phases derived from WAXS (i.e. crystalline, isotropic and oriented non-crystalline phases) and the three phases derived from thermal analysis (i.e. crystalline, mobile and rigid amorphous phases) for PET and Nylon-6 fibers [5,7]. Murthy explains that they do not have any clear evidence that the anisotropic and isotropic non-crystalline components are two distinct phases [7]. Wunderlich proposed in some cases that the intermediate phase could be recognized as the RAF [1].

This work aims to make progress in this area by comparing the mechanically induced structural changes of two polyesters, PET and poly (ethylene terephthalate)-glycol (PETg). These two polymers have close chemical structures but different ability to crystallize. It has been shown that PETg can crystallize only 3% in mass while the crystal content can reach around 40% for PET [17]. By comparing the structural changes of PET and weakly-crystallizing PETg as a function of draw ratio, we expect to have a best-understanding of the non-crystalline component as a function of crystal content. WAXS is used to characterize crystals, isotropic and oriented amorphous phases. Temperature Modulated Differential Scanning Calorimetry TMDSC allows to evaluate the fraction of crystals, mobile and rigid amorphous fractions (MAP and RAF respectively). The comparison of the “microstructural” and the “thermodynamic” three phase descriptions will bring us some news insights of the non-crystalline regions of drawn polyesters.

2. Experimental

Amorphous PET samples are taken from an extruded film of 500 μm in thickness provided by Carolex Co. The number-average molecular weight is $\overline{M}_n = 31,000 \text{ g mol}^{-1}$ and the weight-average molecular weight is $\overline{M}_w = 62,000 \text{ g mol}^{-1}$. The density is equal to $\rho = 1.336 \text{ g cm}^{-3}$. PETg (6763 from Tennessee Eastman Co.) is used as an amorphous statistic copolymer. It consists of cyclohexane dimethanol, ethylene glycol and terephthalic acid with a molar ratio of approximately 1:2:3. PETg could be also described is a random copolymer consisting of 33 mol% poly(1,4-cyclohexylenedimethylene terephthalate) (PCT)

and 67 mol% PET [18]. PETg plates ($4 \times 4 \times 0.2 \text{ cm}^3$) are obtained from pellets by injection molding. The number-average molecular weight is $\overline{M}_n = 26,000 \text{ g mol}^{-1}$, the density is equal to $\rho = 1.27 \text{ g cm}^{-3}$. Uniaxially drawing experiments are conducted on an Instron tensile machine (Model 4301), equipped with a temperature-controlled oven. Samples are drawn at an initial strain rate of 0.14 s^{-1} at $100 \text{ }^\circ\text{C}$. Prior to testing, samples are systematically held for 5 min at $100 \text{ }^\circ\text{C}$ in order to insure thermal stabilization. The drawing temperature is chosen between the glass transition temperature and the PET cold crystallization temperature to avoid thermal crystallization during mechanical experiments. After drawing, the material samples are cold air-quenched down to room temperature before unloading sample in order to prevent chain relaxation [7].

The samples are analyzed using TMDSC TA Instruments DSC 2920. The specific heat capacities for each sample are measured using sapphire as a reference. The sample masses are chosen to be similar to the sapphire sample mass, i.e. approximately 20 mg. The TMDSC experiments are performed with an oscillation amplitude of 0.318 K, an oscillation period of 60 s and with a heating rate of 2 K min^{-1} . These experimental parameters correspond to the “heat only” mode and give the best signal to noise ratio obtained with the apparatus used. The complete deconvolution procedure proposed by Reading et al. is used to determine the reversing and non-reversing parts of the Heat Flows [19,20]. TMDSC allows separating thermal events from kinetic events. Crystallization and melting phenomena are analyzed on the non-reversing Heat Flow signal, while the glass transition can be analyzed for each material regarding to the reversing Heat Flow signal.

Ex-Situ wide angle X-ray diffraction experiments are performed using a Genix microsource X-ray generator operated at 50 kV and 1 mA. The Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) is collimated with a FOX2D mirror and two pairs of Scatterless slits from Xenocs. The 2D-patterns are recorded on a CCD camera from Photonic Science. Both incoming and transmitted intensities are measured with WAXS data acquisition. Thereby, all the X-ray patterns are normalized using the transmission factor, defined as the ratio between the transmitted and the incident intensities. Radial intensity profiles, $I(2\theta)$, are obtained by azimuthal integration of the 2D-patterns from $\varphi = -90^\circ$ to $\varphi = +90^\circ$ by means of the FIT2D software. Quantitative analyses have been performed over the 2θ range $5^\circ < 2\theta < 40^\circ$ using PeakFit software, assuming Gaussian profiles for all scattering peaks and amorphous halos. The weight fraction of the crystalline phase X_c is determined from the ratio of the specific scattering contribution of the crystal phase to the total scattering area. The crystallite size along the directions normal to the plane (hkl), L_{hkl} , is calculated using the Scherrer equation [21]:

$$L_{hkl} = \frac{0.9 \times \lambda}{\cos \theta_{hkl} \times \Delta \theta_{hkl}} \quad (1)$$

where λ is the X-ray wavelength, $\Delta \theta_{hkl}$ is the full-width at half-maximum (FWHM) of the crystalline peak, and θ_{hkl} is the peak position. The PET unit cell used in this work is the one determined by Daubeny et al. [22]. The crystallo-

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