

In situ study of the tensile deformation micro-mechanisms of semi-crystalline poly(ethylene terephthalate) films using synchrotron radiation X-ray scattering

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ABSTRACT

Wide - and small-angle X-ray scattering are used to perform *in situ* experiments with synchrotron radiation. The high X-ray intensity enabled the study of the deformation mechanisms of poly(ethylene terephthalate) semi-crystalline films under tension. Microstructural parameters such as crystallinity ratio, macromolecular orientation, long period, length, width and thickness of crystalline lamellae are measured. A new method to follow macromolecular orientation is detailed. In the elastic-viscoelastic region, lamellae rotate along the tensile axis without increase of orientation parameters. The plastic strain is initiated by crystallographic processes: crystal slip with (010)[001] and (010)[010] systems, flexural breaking of the longitudinal lamellae and separation of (010) planes in transverse lamellae. The plastic flow is the continuation of these processes and the strengthening of the macromolecular orientation in both crystalline and amorphous phases. The shear forces applied to transverse lamellae rotating to a longitudinal orientation make them adopt a tilted shape.

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1. Introduction

Poly(ethylene terephthalate) (most commonly referred to as PET) is a semi-crystalline polyester mainly used for its good electrical insulation and mechanical properties, temperature resistance and permeability [1–3]. Having relatively slow crystallization kinetics, it became a first-class polymer as it can be processed into a large array of controlled microstructures. Biaxially-stretched PET films, similarly to the well-known trade name Mylar, have many applications in various fields such as electronics, packaging or medicine thanks to its biocompatibility. Depending on the process of biaxial stretching (simultaneous or sequential) and the machine and transverse draw ratios, these films can have very different microstructures and thus very different mechanical properties [4–12].

Microstructure and mechanical properties are indeed closely related, a change in the first will directly translate into a change in the latter. The deformation micromechanisms are responsible for

the relation between the microstructure and the mechanical properties. Deformation micromechanisms are defined as the evolution (or adaptation) of the microstructure to an applied load or strain. Wide-Angle X-ray Scattering and Small-Angle X-ray Scattering (abbreviated WAXS and SAXS) are able to evidence a wide array of mechanisms and so have been extensively used for the past twenty years to study the deformation micromechanisms of semi-crystalline polymer under tension. This was possible thanks to the development of new-generation synchrotron light sources for materials' characterization which provide an excellent time resolution for *in situ* experiments [13,14]. *In situ* experiments are necessary in order to accurately study the deformation mechanisms in polymers as opposed to *post mortem* experiments. A number of studies have shown modifications of the crystallinity ratio and amorphous phase orientation during stress relaxation of PET. This is a direct consequence of the formation and conversion of the transient mesophase formed during stretching above the glass transition temperature [15–18].

The tensile stretching of semi-crystalline polymers generates orientation of the macromolecules along the tensile direction both in the amorphous and crystalline phases. Macromolecular orientation is a fundamental aspect of the deformation mechanisms in

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polymers and so has been the main topic of multiple studies [19–23]. On the one hand, the orientation of the amorphous phase produces transitory phases that were evidenced in some polymers (e.g. in PET [24], polylactide [25], polypropylene [26,27] and poly(trimethylene terephthalate) [28]) and are associated to the strain-induced crystallization at temperatures above the glass transition temperature [29,30]. On the other hand, the strain transmitted to the crystalline lamellae generates distortions of the crystal lattice that were described earlier in polyethylene by Pope and Keller [31]. The consequence of such crystallographic processes are lamellar fragmentation [32,33], crystalline phase transformations (e.g. in nylon 6 [34,35] and polyvinylidene fluoride [36]) and martensitic-like phase transformation (e.g. in high-density polyethylene [14]). A number of papers have also used SAXS in order to measure the volume damage (or cavitation) occurring during the tensile stretching of semi-crystalline polymers [32,37–41]. The technique gives access to the size and shape of the forming cavities which makes possible the determination of the intrinsic mechanical behavior of materials [41].

This paper aims at quantitatively study the deformations mechanisms in the elastic-viscoelastic and plastic domains of biaxially-stretched PET films under tension using synchrotron-radiation X-ray scattering. The combination of WAXS and SAXS enables a multi-scale analysis, from the crystallographic spacing distances up to the crystallite size (from a few Ångströms up to a few dozen nanometers). The evolution of the orientation of the polymer chains and the crystalline lamellae, crystallinity ratio, crystallite size and shape, spacing of specific crystallographic planes as a function of the applied true strain will be measured and discussed. The underlying mechanisms will be eventually identified and explained.

2. Materials and methods

2.1. Polyethylene terephthalate (PET) films

The materials investigated are semi-crystalline polyethylene terephthalate films having a thickness of 36 μm . Their density is $\rho = 1.393 \text{ g cm}^{-3}$. The temperature of the α -relaxation associated to the glass transition measured by dynamic mechanical analysis at 1 Hz is $T_\alpha = 119^\circ\text{C}$ at the maximum of the loss tangent peak. The melting temperature measured by differential scanning calorimetry is $T_m = 255^\circ\text{C}$ at the maximum of the melting endotherm. The crystallinity ratio is $\chi_c = 0.43$, calculated with a melting enthalpy of

a perfect crystal of 140 J/g [42]. The polymer chains in the crystallite phase are arranged in a triclinic lattice system having the following parameters: $a = 0.456 \text{ nm}$, $b = 0.594 \text{ nm}$, $c = 1.075 \text{ nm}$, $\alpha = 98.5^\circ$, $\beta = 118^\circ$, $\gamma = 112^\circ$ [43].

2.2. Sample preparation

The specimens are strips of $50 \times 10 \text{ mm}^2$ with a round defect as shown on Fig. 1(a). The defects located at the center of the specimens are symmetrical circular segments cut from the strips in order to produce a reduction of the cross-section and ensure the localization of the plastic strain in the scattering volume. The effective length is 30 mm. Two pieces of adhesive copper tape were placed at the center in order to measure the local strain from the video-recorded experiments. Because previous WAXS experiments showed an initial orientation of the chain segments in the crystalline phase, it was decided to cut samples along the longitudinal and transverse directions (parallel and perpendicular to the macromolecular orientation, respectively). The longitudinal and transverse samples will be noted LD and TD samples.

2.3. In-situ tensile tests

The samples were continuously strained at room temperature with a Kammrath & Weiss tensile micro-machine using a crosshead speed of 20 $\mu\text{m/s}$ in the elastic-viscoelastic domain and 12 $\mu\text{m/s}$ in the plastic domain. The crosshead speeds were calculated according to the true mechanical behavior at a constant true strain rate of 5.10^{-4} s^{-1} determined with the VidéoTraction™ system. This is a video-controlled tensile test during which the displacement of markers defining a Representative Volume Element (RVE) is recorded [44,45]. The cross-head speed is adjusted in real-time as to obtain a constant true strain rate inside the RVE. For samples having a very low thickness-to-width ratio, the hypothesis are those of isochoric plane tension [46]: the transverse strain ϵ_{22} in the RVE is zero and the volumetric strain $\epsilon_v = \epsilon_{11} + \epsilon_{22} + \epsilon_{33}$ is always null. As a consequence, the axial strain ϵ_{33} in the RVE is equal to the opposite of the normal strain ϵ_{11} in the RVE. The resulting axial load in the RVE is thus calculated using Equation (1):

$$\sigma_{33} = \frac{F}{S_0} \exp(\epsilon_{33}) \quad (1)$$

where F is the applied force and S_0 is the initial cross-section.

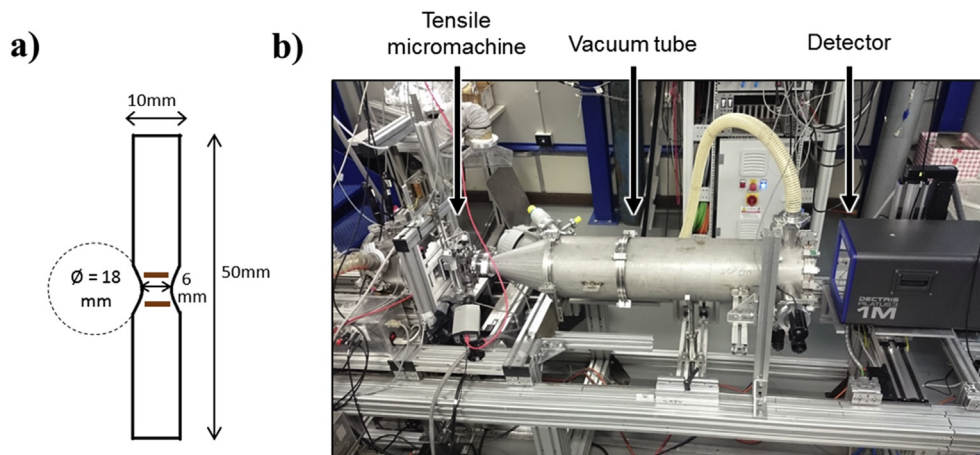


Fig. 1. (a) Schematic representation of the sample dimensions. (b) Photograph of the experimental setup in the SAXS configuration (SAXS beamline at Elettra Sincrotrone Trieste, Italy).

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