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Dependence of conformational relaxation on nanoconfinement in semicrystalline poly(ethylene terephthalate)

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ABSTRACT

Novel aspects concerning the micromechanical response of amorphous regions confined by crystals in nano-sized domains are illustrated for semicrystalline poly(ethylene terephthalate) (PET), on the basis of microindentation hardness and dynamical mechanical spectroscopy (DMS) analyses ($10^{-3} \div 60$ Hz frequency range for DMS). PET samples were crystallized from the glassy state at low and high temperatures ($T_c = 100$ °C and 160 °C, respectively) and subsequently recrystallized some degrees above to gain information on the nature of the amorphous regions. DMS at 95 °C reveals two segmental relaxation processes ascribed to the interlamellar amorphous regions (slow mode) and to the interstack amorphous pockets (APs) (fast mode) respectively, the latter being the object of the present study. It is shown that recrystallization changes the cooperativity within the APs. At low T_c, an increase in the cooperativity and the free energy barrier for readjustment is found after recrystallization. Room temperature indentation measurements reveal an enhancement of the average hardness value of the amorphous regions, H_a, on samples recrystallized a few degrees above $T_c = 100$ °C. The reduced size of the APs regions upon recrystallization is discussed as a relevant parameter giving rise to an enhanced segmental confinement and a parallel hardening. Results for the high T_c material reveal that, in this case, both the cooperativity (measured at 95 °C) and H_a (measured at room temperature) decrease upon recrystallization. The influence of the coupling of the APs with the crystal walls, on the relaxation mode and in turn on the mechanical behavior of the material, is envisaged to be a possible mechanism underlying these observations.

1. Introduction

Understanding how nanoconfinement affects the bulk properties of physical systems is of extreme importance from the viewpoints of, both, basic physics and related technological aspects. In Polymer Science, the relevance of the nano-confinement of the amorphous domains in the overall mechanical and dielectric responses has been addressed in preceding studies (Baltá-Calleja et al., 2007, 2009; Pieruccini et al., 2008; Pieruccini and Ezquerra, 2009). Poly(ethylene terephthalate) (PET) has been frequently employed to contrast experimental observations with a number of models developed to understand the nature of the amorphous regions.

At the end of the crystallization process, nano-sized amorphous domains remain embedded by the crystals (Strobl, 1997). Under these conditions, a sort of crystal/amorphous equilibrium is established and the thermodynamic state of the amorphous regions necessarily carries information about the thermodynamic state of the embedding crystals (Pieruccini and Flores, 2010). The latter can be easily described (Hoffman, 1958) and hence, this scenario offers some advantage with respect to the study of polymers confined in other media such as for example in nanoporous glasses (see e.g. Schick, 2005).

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Isothermal crystallization processes lead to the formation of lamellar stacks with morphological features characteristic of the crystallization conditions. Upon further heating, the stacks loose stability, which may be subsequently recovered by re-crystallizing into new lamellar stacks with different crystalline and amorphous layer thicknesses. For instance, in case of PET crystallized from the glassy state, a low-temperature melting endotherm appearing a few degrees above the crystallization temperature is frequently associated to recrystallization processes (see e.g. Fig. 1 in Flores et al. (2008)).

The aim of the present study is to explore the influence of recrystallization processes on the mechanical performance of PET as a consequence of variations in the confinement of the amorphous regions by the lamellar crystals. For this purpose, PET crystallized from the glassy state at two different temperatures (100 °C and 160 °C) and further recrystallized in the vicinity of the respective low-temperature melting endotherms will be examined. Microindentation hardness will be used to explore the differences in the mechanical properties of the amorphous regions induced by the various thermal treatments. This technique is based on the optical measurement of residual indentations with depths in the micrometer range, hence, involving the deformation of thousands of lamellar stacks. Average values of the hardness of the amorphous and the crystalline regions can be achieved assuming well established relationships between microhardness and characteristic structural parameters (Baltá-Calleja and Fakirov, 2000). Morphological and structural changes taking place at nanometer scale either in the crystalline or in the amorphous regions can be readily detected by means of microindentation hardness (Baltá-Calleja and Fakirov, 2000). For example, in case of glassy polymer domains, microhardness has been proved to be sensitive to physical ageing, chain orientation and local internal order (Baltá-Calleja and Fakirov, 2000; Flores et al., 2009). In addition, dynamic mechanical spectroscopy (DMS) analysis will be employed to extract information on the extent of segmental confinement within the amorphous regions upon recrystallization. Indentation hardness and spectroscopy measurements will be comprehensively discussed in the light of the structural information provided by means of wide-angle X-ray diffraction and with the help of preceding published small-angle X-ray diffraction data.

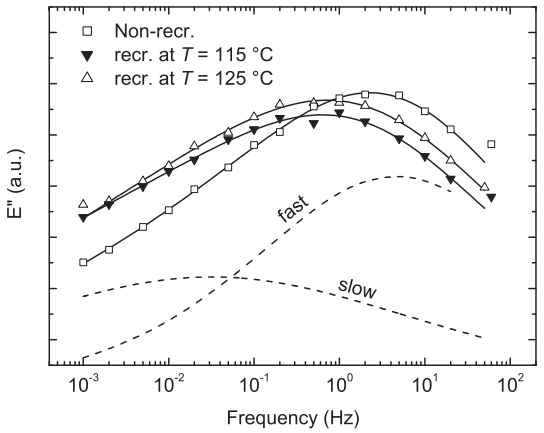

Fig. 1. Imaginary part of the mechanical modulus E'' at $T = 95$ °C, as a function of the frequency, for a PET sample crystallized at $T_c = 100$ °C and subsequently recrystallized. The solid line is the fitting curve resulting from the superposition of two symmetric Havriliak–Negami processes labeled as Fast and Slow, represented by dashed lines for the non-recrystallized sample. (Replotted from Flores et al. 2011)

2. Experimental

Glassy PET from Goodfellow (ES 301465) with molecular weight Mw∼20.000 g/mol was purchased in form of films of 0.5 mm thickness. Portions of the films were crystallized in inert atmosphere at either T_c =100 °C or 160 °C for 7 h. The specimens were investigated without further treatment and also after recrystallization at 115 °C or 125 °C in case of the sample crystallized at 100 °C, and at 175 °C and 185 °C for the material crystallized at 160 °C. All recrystallization treatments were applied under vacuum for a period of 2 h.

Wide-angle X-ray scattering (WAXS) measurements were carried out at room temperature using a Micro Star rotating anode generator with copper target manufactured by Bruker (Germany). WAXS patterns were recorded using a Mar345 image plate with a resolution of 3450×3450 pixels and 100 μm/pixel; a sample-to detector distance of 200 mm was used. Isotropic rings associated to the diffraction maxima were obtained for all the samples. In case of the untreated PET sample, an amorphous halo characteristic of the glassy material was obtained. All patterns were azimuthally integrated using the FIT2D software package in order to obtain intensity curves as a function of diffraction angle (Hammersley et al., 1994). The degree of crystallinity, α, was estimated by fitting the amorphous halo of glassy PET to the diffraction curve of each crystallized material. The α values were determined from the ratio of the area under the crystalline peaks to that of the total diffraction curve. In the derivation of α, an angular range from 5° to 40° (2θ), covering the first order of the amorphous halo and the most intense crystalline peaks was considered.

Microindentation measurements were performed at room temperature using a Vickers diamond attached to a Leica tester. The indenter penetrates the sample surface at a given load, P, for a short period of time (6 s) to minimize creep effects. The diagonal of the residual impression, d, left behind upon load release, is measured using an optical microscope. Microhardness values, H, are derived following:

$$H = 1.85\frac{P}{d^2} \tag{1}$$

A load of $P = 0.98$ N was employed. Indentations with diagonal lengths in the range of 100 μm were obtained. Microhardness values were determined from the measurement of at least 8 indentations. Similar indentation tests using loads of 0.49 N and of 0.25 N yielded the same H values within the error.

Isothermal DMS analysis was performed with a TRITON Technology Analyser in the frequency interval of