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SAXS study on the crystallization of PET under physical confinement in PET/PC multilayered films

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ABSTRACT

The present work is concerned with the study of the development of the crystalline structure of poly(ethylene terephthalate) in multilayered films of poly(ethylene terephthalate)/polycarbonate (PET/PC) prepared by means of layer multiplying coextrusion. Small angle X-ray scattering patterns were recorded during isothermal crystallization experiments and evaluated by means of Ruland's interface distribution function. Thus, structural parameters describing the thickness distribution of crystalline and amorphous layers were determinated. It is shown that the crystallization of PET is delayed with increasing confinement. However when the crystallization process comes to an end, the values of the nanostructural parameters of the lamellar system are nearly the same for the confined and non-confined PET.

1. Introduction

It is well known that a reduced dimensionality of materials may result in interesting phenomena. In particular, for polymer systems it has been found that confinement can change the glass transition temperature [1–4], molecular mobility [5,6], behaviour of the phases and morphology [7,8], molecular orientation [9] and crystallization behaviour [10–13]. Polymeric materials can be subjected either to chemical or to physical confinement. Whereas physical confinement is only restricting the volume of the material, chemical confinement is restricting as well, molecular motions by chemical bonds [14].

The crystallization of polymers in physically confined environments is a topic of increasing interest because of the required basic understanding of crystallization in the application of polymers for nanotechnologies. In studies of confined crystallization of polymers, very particular effects have been found. The mechanisms of nucleation are affected due to the reduced number of chain conformations and interacting molecules in comparison with the bulk [11]. Lamellar growth rate and the final degree of crystallinity are diminished if the chains in thin polymer films are subjected to a preferred orientation [10,15]. Confined crystallization of polypropylene layers in between amorphous layers of polystyrene results in discoidal morphologies which transform into long stacks of very short lamellae arranged in fan-like arrays, when decreasing layer thickness from the microscale to the nanoscale [16]. The physical confinement of poly(ε-caprolactone) (PCL) in blends with a lamellar morphology of poly(ε-caprolactone)/poly(styrene)-*b*-poly(ethylenepropylene) (PCL/PS-PEP) has shown to affect both the morphology and the orientation of PCL crystals [14].

Confined polymer layers are readily prepared by layer multiplying coextrusion technique, which can produce laminar architectures up to thousands of layers [17,18]. The thickness of the individual layers of these multilayered films can be tuned from the micrometer to the nanometer range, being proven that they are very suitable materials to study the effects of physical confinement on the structure formation of semi-crystalline polymers [16,19]. Two immiscible polymers, poly(ethylene terephthalate) (PET) and polycarbonate (PC), have been used to fabricate the multilayered films. A previous investigation of the nanostructure of PET in the confined state under physical confinement, performed on annealed PET/PC multilayered films [20], has already shown that, with increasing confinement (i.e. when the PET layer becomes thinner), the volume crystallinity of the selectively crystallized PET layers decreases. Furthermore, confinement induces an increase of the long period (i.e. the distance between neighboring crystalline lamellae) of semi-crystalline PET. These effects are observed when

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the thickness of the PET layers becomes smaller than 1 μm. The crystallization temperature at which drastic changes between confined and non-confined PET were found is 117 °C.

The aim of the present study is to investigate the evolution of the nanostructure. For this purpose the real time small angle X-ray scattering (SAXS) method is used to monitor the isothermal crystallization of PET confined between amorphous layers of PC. For data analysis, the scattering patterns are transformed into Ruland's interface distribution function (IDF) [21]. The IDF, $g(r)$, represents the probability distribution of finding two interfaces between a crystalline and an amorphous lamella at a certain distance r. The IDF can be fitted by models which describe the sizes and the statistical arrangement of the lamellae in the material [22,23]. In this way the structural parameters are determined. Parameters of interest are the average thickness of crystals, l_c, the thickness of the amorphous region between crystals, l_a, and the long period, L (average distance between adjacent lamellar crystals). As far as we know this is the first time that structural parameters for polymer nanolayered systems are reported.

2. Experimental section

2.1. Materials

The materials used in this work are commercial thermoplastic polyesters: poly(ethylene terephthalate) (PET) (M&G Cleartuf 8004) and polycarbonate (PC) (DOW Calibre 200-10). Both materials have a molecular weight of 30 000. PET/PC multilayered films with 1024 layers, total thickness of ~75 μm and PET/PC volume ratios of 100/0 (pure PET), 70/30, 50/50, and 30/70 were fabricated by means of layer multiplication coextrusion technique described elsewhere [22]. The thicknesses of the individual PET layers are 70 nm for the coextruded PET (100/0) film, and 100, 70 and 50 nm for the 70/30, 50/50 and 30/70 PET/PC coextruded multilayered films respectively. As a matter of fact, the coextruded pure PET film loses the layered structure during processing and finally behaves as bulk PET. The as-processed multilayered films were in the glassy-amorphous state. The PET layers of the composite can be crystallized selectively by thermal treatments, while the PC layers remain in the amorphous state, because the glass transition temperature of these polymers is quite different (75 °C for PET and 150 °C for PC). Thus, the changes occurring in the nanostructure of PET during crystallization in a physically confined environment have been studied.

2.2. SAXS measurements

Time-resolved SAXS experiments during isothermal crystallization at 117 °C were performed at the beam line A2 at HASYLAB, Hamburg (Germany) using synchrotron radiation of 0.15 nm. The multilayered films were mounted in the furnace of the beam line A2 [24] in normal transmission geometry, i.e. the film surface normal was parallel to the X-ray beam. As we knew already from a study [20] in this geometry the recorded SAXS patterns always look as if the material were isotropic. The scattering patterns of the machine background and of the samples were exposed for 120 s and recorded on a two-dimensional MAR-CCD-165 detector placed at a distance of 2050 mm from the sample. The distance was verified by means of the scattering from a rat-tail tendon standard. The flux of the primary beam was measured before and after penetrating the sample.

2.3. SAXS analysis

All two-dimensional scattering images were normalized for detector efficiency, incident beam flux, and exposure time. The machine background was multiplied by the sample absorption and subtracted. The first pattern of each series taken at 117 °C still showed the diffuse scattering of an amorphous sample (I_o). It was used as an amorphous background and subtracted from each of the following patterns. Thus, a pre-evaluated scattering intensity of the semi-crystalline nanostructure, $\lceil I(\mathbf{s})\rceil_2(s_1,s_3) := \lceil I\rceil_2(s_1,s_3)$, was obtained. Here $\mathbf{s}=(s_1, s_2, s_3)$ is the scattering vector with its modulus $s=|\mathbf{s}|=(2/\lambda)\sin\theta$, λ is the X-ray wavelength and 2θ is the scattering angle. Because the X-ray beam is parallel to the normal surface of the multilayered films (s_2-direction) not the complete scattering $I\,(\mathbf{s})$ in reciprocal space is measured, but only the intensity $\lceil I\rceil_2(s_1,s_3)$ in the (s_1, s_3)-plane.

As it has been shown in a previous work [20], the irradiation in s_1-direction (i.e. parallel to the film surface), $\lceil I\rceil_2(s_2,s_3)$ generates completely different scattering patterns showing a strong equatorial streak from the multilayer structure and an anisotropic scattering, when PET is crystallized in the thinner layers. Therefore, it is impossible to record the complete scattering $I(\mathbf{s})$ in the time-resolved experiment and we have to resort to the nanostructure information contained in $\lceil I\rceil_2(s_1,s_3)$. According to scattering theory [23] the two-dimensional Fourier transformation, $\Im_2()$, of the measured intensity is related to the two-dimensional projection, $\{\ \}_2$, of the correlation function $P(r)$ in real space $\{P\}_2(r_1,r_2) = \Im_2(\lceil I\rceil_2(s_1,s_3))$. Ultimately, our analysis remains limited to variations of this projected nanostructure information.

The measured intensities $\lceil I\rceil_2(s_1,s_3) = \lceil I\rceil_2(s_{13},\phi) = \lceil I\rceil_2(s_{13})$ were always found to be isotropic in the measured (s_1, s_3)-plane. Here $s_{13} = (s_1^2+s_3^2)^{0.5}$ and $\phi = \arctan(s_3/s_1)$ is the azimuthal angle. Thus, taking advantage of the available two-dimensional data, we carried out azimuthal averaging $\lceil I\rceil_2(s_{13}) = 1/(2\pi s_{13}) \int_0^{2\pi} \lceil I\rceil_2(s_{13},\phi)\mathrm{d}\phi$ in order to increase the signal-to-noise ratio in the resulting scattering curve.

We are assuming that the emerging scattering is related to the semi-crystalline nanostructure of a lamellar system. In such a system the scattering of each layer stack is described by a one-dimensional intensity $I_1(s_x)$, with s_x the direction normal to the lamellae. If the orientation distribution s_x of the layer stacks were completely at random, we would observe an isotropic scattering, $I(s)$, and the representative one-dimensional scattering is obtained by solid-angle integration, which is simplified as:

$$I_1(x) = 2\pi s^2 I(s) \tag{1}$$

for isotropic scattering in three-dimensional space. Equation (1) is called Lorentz correction [23]. Although our data are only isotropic in two dimensions, we followed the usual method, carried out a Lorentz correction $\tilde{I}(s_{13}) = s_{13}^2\lceil I\rceil_2(s_{13})$ and determined a long period $L = 1/s_{13m}$ from s_{13m}, the position of the peak maximum in this curve. Bearing in mind the above-mentioned relations we will, in general, use a simplified notation, e.g. $I(s)$ instead of $\lceil I\rceil_2(s_{13})$.

From $I(s)$ an interface distribution function [21] $g(r)$ was computed considering $I(s)$ as a one-dimensional section in reciprocal space that was measured by a point focus. The evaluation of these one-dimensional curves was carried out by the program TOPAS [25]. The first step was the determination of the deviations [26] from the ideal Porod's law. For this purpose $\ln(s^4 I(s))$ was plotted vs. s^2 [23]. From slope and intercept of the Porod-line the parameters A_P (Porod asymptote) and d_z (width of the transition zone at the interface of the crystalline lamella between crystalline and amorphous density) were determined. With these parameters the interference function of ideal lamellar two-phase system $G(s) = s^4 I(s)\exp[(4/9\pi^2 d_z^2 s^2)] - A_\mathrm{P}$ was computed. The one-dimensional Fourier transform of $G(s)$ is the interface distribution function