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Surface crystallization of poly(ethylene terephtalate) studied by atomic force microscopy

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Abstract

Poly(ethylene terephtalate) (PET) crystallization was shown by atomic force microscopy (AFM) to occur at 85 °C in the first few nanometers near the polymer–air interface. The surface was fully transformed into spherulites after 30 min, while no signs of bulk crystallization were observed by FTIR. All the observed spherulites presented a nucleation centre, indicating that the crystallization process started at the surface of the film. Tapping mode AFM confirmed that the spherulites were not covered by an amorphous layer. The most probable explanation is a decrease of T_g near the surface. Due to the poor crystallization conditions, the constitutive units of the spherulites were small crystalline blocks. By changing the annealing time, it was possible to produce PET surfaces with different surface fractions consisting of semi-crystalline material (spherulites) and amorphous matrix. This provided a controlled surface heterogeneity on the submicrometer scale, with a contrast in terms of stiffness, roughness and swelling by organic solvents. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Atomic force microscopy; Crystallization; Surface

1. Introduction

Crystallization of polymers, and of poly(ethylene terephtalate) (PET) in particular, has been studied since a long time. Early studies [1] were purely descriptive and dealt with the influence of crystallization temperature on the morphology of the lamellae, fibrils and spherulites. Later on, experiments were done in order to elucidate the mechanisms of crystallization and the influence of the thermal history [2–4] and also of stretching [5–7]. In the last few years, more applied studies appeared, dealing with the influence of solvent on crystallization, the measurement of Young modulus [8] of the two phases, the nanotribology of films [9], etc.

Most studies concerned crystallization in the bulk. The samples were studied with global methods such as DSC, IR, X-ray diffraction which do not discriminate between phenomena occurring in the bulk and at the surface. Direct observation of the morphology by TEM, SEM or atomic force microscopy (AFM) was done on ultra-thin sections [10] or on sample surfaces [11], considering in the latter case that the observations made at the surface may be extrapolated to the bulk.

Recently, surface crystallization was considered specifically. Hayes et al. [12] compared the kinetics of surface and bulk crystallization and showed that surface crystallization was a faster process. Lippitz et al. [13] studied biaxially stretched and amorphous PET by a surface sensitive method (near-edge X-ray absorption fine structure, NEXAFS) which allows a discrimination to be made between the two physical states of the material.

In the work presented here, we studied the crystallization of solvent-casted PET films at 85 °C using mainly AFM. We show that the surface of the film can be completely constituted by spherulites although no crystallization is detected in the bulk. We bring evidence that, under the processing and temperature conditions used, the crystallization process starts at the surface, thus providing a material with spherulites cropping out at the surface.

2. Experimental

2.1. PET films preparation

PET was provided by ICI (Everberg, Belgium, ref BL90,

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$M_w = 39690, T_g = 75\,^\circ C,\ T_m = 250\,^\circ C,\ d = 1.38\ g/cm^3$). Films of 3.7 μm thickness were prepared by solvent-casting of 1 wt% polymer solution in hexafluoroisopropanol 99.5 + % (Aldrich, Bornem, Belgium; ref RTTP02500). Fifty microlitres of solution were entirely spread on a 15 mm diameter glass coverslip (Vel, Leuven, Belgium; ref 1502470) in a nitrogen atmosphere at 25 °C and the solvent was allowed to evaporate during 2 min. Then the samples were put in an oven at 40 °C for 7 days to evaporate remaining traces of solvent. Finally, the films were annealed during given times in an oven at 85 °C, unless otherwise stated.

2.2. Atomic force microscopy imaging

AFM measurements were performed at room temperature in air using a commercial optical lever microscope (Nanoscope III, Digital Instrument, Santa Barbara, CA). Contact mode topographic and lateral force images were recorded using oxide-sharpened Si_3N_4 microlevers (C to E triangular cantilevers; ref MSCT-AUHW; Park Scientific Instruments, Mountain View, CA) with a radius of curvature of 20–60 nm and a spring constant ranging from 0.01 to 0.1 N/m. The imaging force was kept as low as possible and the scan rate was 4 Hz. When needed, friction images were recorded at the same time in trace and retrace direction.

Tapping mode height and phase images were recorded with etched silicon probes (ref TESP7, Digital Instrument, Santa Barbara, CA) with a force constant of 20–100 N/m and a resonance frequency of 195 kHz. Free amplitude (A_0) and set point amplitude (A_{sp}) were modified according to the experimental requirements. The scan rate was 1 Hz.

2.3. Image analysis

Image analysis was performed to obtain the surface fraction consisting of spherulites, using the software Visilog 5.2 Advanced (Noesis, Courtaboeuf, France). Therefore, friction images were used as they give a good contrast and a great number of images can be saved in a reasonable time. All images (256 × 256 pixels) were recorded at a scan rate of 4 Hz. Since the friction contrast increases as the lever becomes more flexible, C probe was always used. The $10 \times 10\ \mu m^2$ image size gave the suited compromise between the number of observed spherulites and their resolution.

For each sample, three images were treated as follows. A grey scale threshold was applied to the raw image (Fig. 1(a)) to give a binary image (Fig. 1(b)). In order to clean the background, an erosion was applied (Fig. 1(c)); this operation consists in erasing any pixel in contact with a pixel that is part of the background. The final image presented in Fig. 1(d), was obtained by reconstruction of the objects left after erosion.

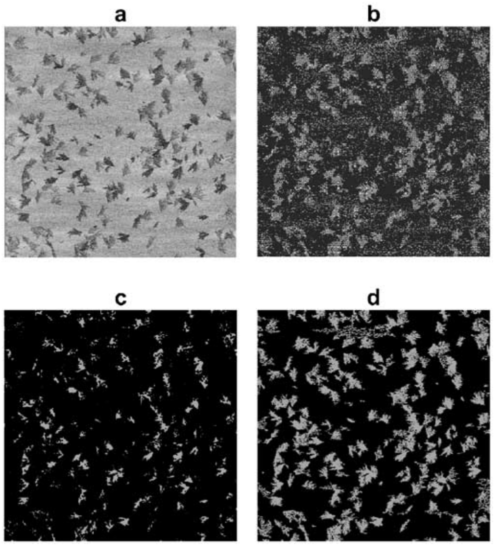

Fig. 1. Stages of the treatment applied to a raw $5 \times 5\ \mu m^2$ AFM image in order to obtain the surface fraction consisting of spherulites: (a) starting image, (b) binarization, (c) erosion and (d) reconstruction.

2.4. Fourier transform infrared spectroscopy

FTIR was performed at room temperature with a Bruker Equinox 55 (Ettlingen, Germany) flushed with dried air. The films were detached from the glass substrata by floating them on water. Fifty scans were accumulated for each sample and the resolution was 1 cm^{-1}.

3. Results

3.1. Crystallization kinetics

Fig. 2 presents $5 \times 5\ \mu m^2$ AFM lateral force images

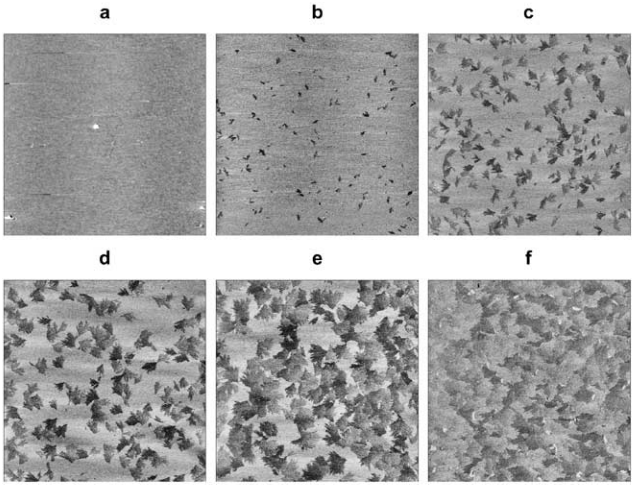

Fig. 2. The $5 \times 5\ \mu m^2$ lateral force images (contact mode) of PET samples annealed at 85 °C for increasing periods of time. (a) None, (b) 5 min, (c) 10 min, (d) 15 min, (e) 20 min and (f) 30 min. Z range: arbitrary units.

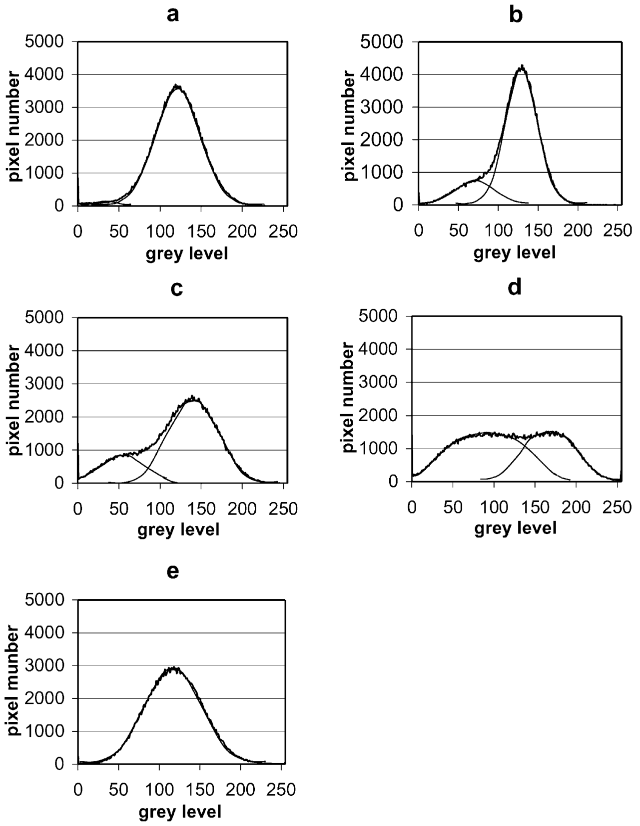

Fig. 3. Histograms of grey levels for samples annealed at 85 °C during (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min and (e) 30 min. The selected threshold was the intersection between the two components.

obtained after different annealing times at 85 °C. The non-annealed sample showed a totally featureless morphology. Upon annealing, spherulites were observed. They were already visible after 5 min. Their size and number raised with time until the surface was completely modified. Due to the low annealing temperature, their density at complete coverage was high and their size reduced, the greatest dimension being about 300–500 nm.

Image analysis was used to measure the surface fraction consisting of spherulites. The histograms presenting the number of pixels in the starting image as a function of grey levels showed two populations as illustrated in Fig. 3, except for the sample annealed for 30 min. The threshold used for binarization was the grey level at the intersection of the two distribution curves. It has to be noted that the absolute values of grey level cannot be compared from one image to another; only the ratio between the two components are relevant in this analysis. Fig. 4 shows that the surface fraction consisting of spherulites evolved nearly linearly with time and reached about 100% after 30 min. It has to be noted that the film was still transparent after 30 min annealing.

The bulk crystallinity of PET was evaluated by comparing the relative intensities of 1410 and 1342 cm^{-1} FTIR peaks [12]. The former is due to the C–H aromatic ring vibration which is insensitive to conformation and can thus be used to correct for slight sample thickness variations. The latter is to be related to the trans conformation of the glycol unit which is characteristic of crystalline PET. Fig. 5 presents FTIR spectra obtained on different samples. The samples annealed for 10 min (b), 30 min (c), 8 h (d) and 24 h (e) presented the same spectrum as the non-annealed sample (a). In contrast, films annealed for the same times at 150 °C ((e)–(i)), which were not transparent, presented a much larger 1342/1410 intensity ratio.

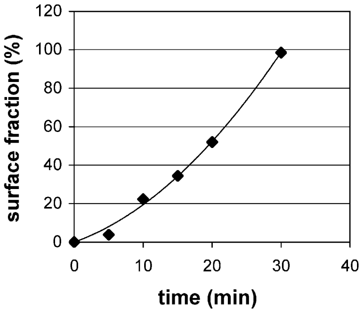

Fig. 4. Evolution of the surface fraction consisting of spherulites as a function of time at an annealing temperature of 85 °C.

3.2. Detailed structure of the spherulites

Since topographic images obtained in contact mode gave very poor resolution (images not shown), tapping mode was used in light tapping conditions (free amplitude $A_0 = 250$ nm, set point amplitude to free amplitude ratio $A_{sp}/A_0 = 0.8–0.9$). Fig. 6(a) shows a representative image and illustrates the particular spherulite morphology. All spherulites possess a centre of nucleation (marked with a white arrow) from which they develop to form crystalline features with a sector like shape. The lamellae start to grow at the centre and, due to the high density of branching, the crystalline features are dense, as shown on the $1 \times 1\ \mu\mathrm{m}^2$

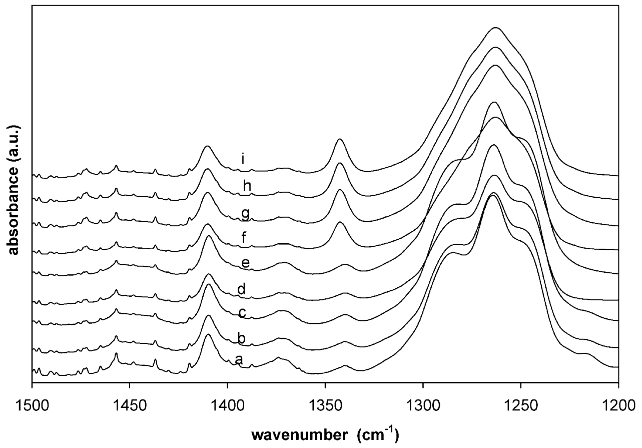

Fig. 5. FTIR spectrum of PET samples. (a) Not annealed; annealed at 85 °C for (b) 10 min, (c) 30 min, (d) 8 h at 85 °C, (e) 24 h; annealed at 150 °C for (f) 10 min, (g) 30 min, (h) 30 min, 8 h, (i) 24 h.

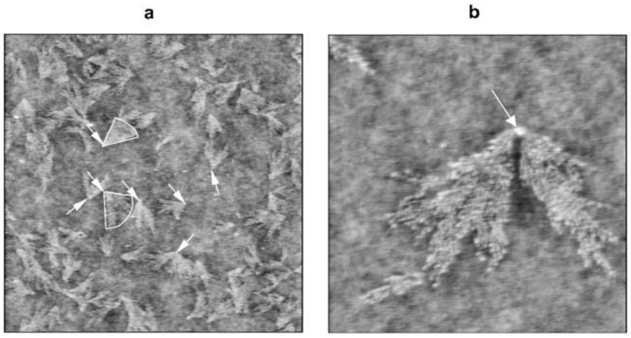

Fig. 6. Detailed AFM (tapping mode) height images of PET samples annealed for 10 min at 85 °C. $5 \times 5\ \mu m^2$ (a) and $1 \times 1\ \mu m^2$ (b) images. Z range: 10 nm. White arrows indicate the centre of nucleation and white lines indicate the overall shape of the spherulites.

image presented in Fig. 6(b). Lamellae seem to be constituted of small aligned blocks and have a width of about 10 nm.

3.3. Difference of properties between crystalline and amorphous materials

Fig. 7 presents a lateral force image of a sample annealed for 10 min, the image (a) being constructed from the trace scan (from left to right), and the image (b) being constructed from the retrace scan (from right to left). The contrast was reversed from one scan direction to the other, indicating that the contrast is due to friction and not to topography. The image resolution was clearly enhanced compared to topographic images even in tapping mode.

Fig. 8 presents topography and phase images obtained in tapping mode. Since it is known that processing parameters can influence the quality of the results, images were taken at A_0 values of 100 (image b), 400 (image c) and 600 mV (image d). For each A_0, the A_{sp}/A_0 ratio was decreased during the image acquisition. Particular attention was paid to the resolution of the spherulites, to the contrast between the crystalline and amorphous phases and to the overall shape of the spherulites. Considering the topography, it is clear that the resolution is better at low A_0 and high A_{sp}/A_0, whereas the contrast and the overall shape of the spherulite remain the same over the whole range of forces. The variation of image quality as function of the interaction force is more visible on phase shift images. At low A_0 and high A_{sp}/A_0 ratio, the contrast is poor and mainly due to edge effect, however, the fine structure of spherulites can be observed; when the A_{sp}/A_0 ratio is reduced the contrast vanishes. At medium A_0, the contrast and resolution are good, the spherulites appearing brighter than the amorphous phase for all the A_{sp}/A_0 ratio values. At high A_0, the contrast is enhanced with the decrease of the A_{sp}/A_0 ratio, and contrast inversions are observed. In all the cases, the overall shape of the spherulite remains unmodified.

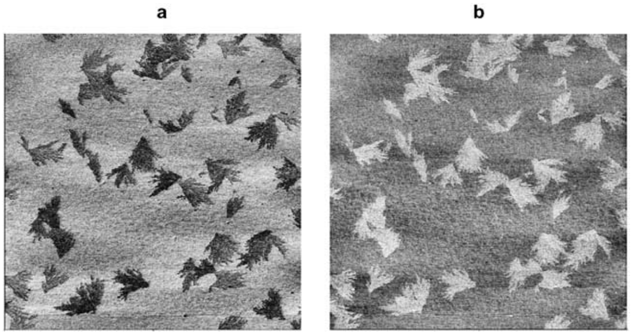

Fig. 7. The $5 \times 5\ \mu m^2$ lateral force images of PET films annealed at 85 °C during 10 min: (a) trace image and (b) retrace image.

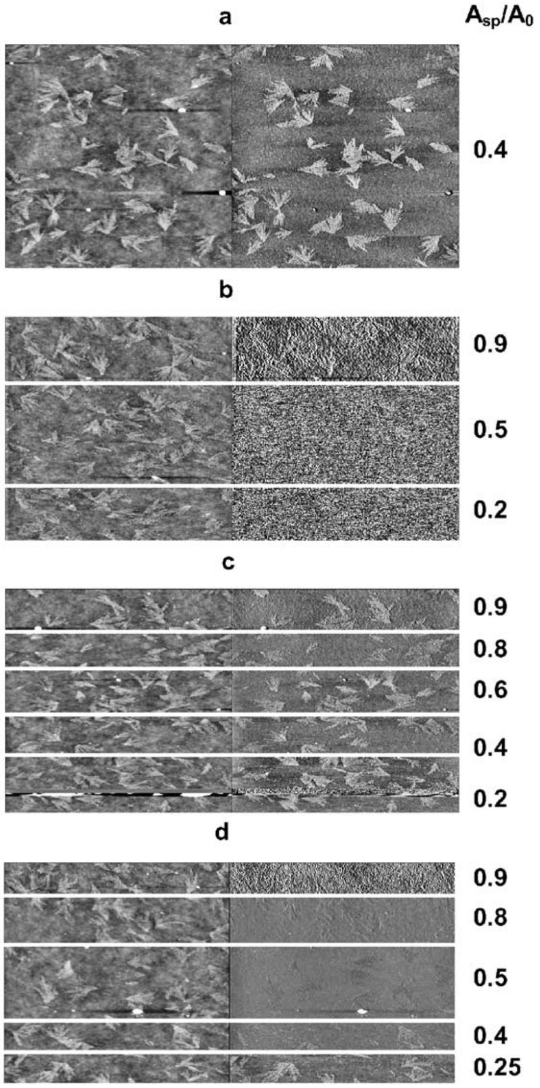

Fig. 8. Phase shift (right) and topography images (left) obtained in tapping mode on a PET film annealed for 10 min at 85 °C. $A_0 = 400$ (a), 100 (b), 400 (c) and 600 mV (d). (b), (c) and (d) images were scanned at decreasing A_{sp}/A_0 ratio as indicated at the right hand side of the images.

4. Discussion

The question of the existence of crystalline material at polymer surfaces is still open. According to numerous authors, spherulites are always covered by amorphous material [14,15]. The results presented here bring several evidences that crystallization is starting at the surface of the polymer film.

FTIR results indicate clearly that the samples examined by AFM are not crystallized in the bulk. On the other hand, AFM images show that crystallization at the surface is very fast, the entire surface being transformed after 30 min. Each spherulite presents a nucleation centre located at the surface and thus starts to grow at the air–polymer interface. A growth from the bulk up to the surface would have created crystalline structures constituted by lamellae which would be radially oriented but would not converge into a centre.

In tapping mode AFM, the phase shift contrast evolves appreciably as a function of the interaction force and thus indentation depth; however, the overall shape of the spherulites remains the same. This means that the crystalline structures crop out at the surface. If it was not the case, the shape would evolve and the size would increase as the interaction force increases [16]. The evolution of the contrast with the imaging conditions may be tentatively explained as follows. In soft conditions, the water layer that covers all the surfaces exposed to ambient atmosphere prevents the tip to be in real contact with the surface; the contrast is then mainly due to topography. When A_0 is increased and A_{sp}/A_0 ratio decreased, the tip can pass through the water layer and probes the viscoelastic properties of the surface; the spherulites then appear stiffer (brighter) than the amorphous matrix. At very high A_0, the inversion of phase contrast is not fully understood; the larger phase shift in the softer amorphous layer may be due to adhesion or viscoelastic effects resulting from greater indentation depth.

From all our observations, it is clear that the spherulites are really cropping out at the surface of the film and that the crystallization process is limited to the surface layer. A possible explanation is that, as observed for other polymers [17], the T_g of PET would be lower in the first few nanometers below the surface. This would make crystallization easier at the surface than in the bulk. While lowering of the T_g may be very small, its effect could be noticeable because of the small difference (10 °C) between the annealing temperature and the bulk T_g.

The granular aspect of the crystalline features observed by AFM may be related to the DSC observation that crystallization from the glassy state at a temperature only slightly higher than T_g gives imperfect crystals [3]. Heck et al. [18] have indeed shown for PP that small crystalline blocks were the first step of the crystallization process; annealing the polymer at higher temperature allowed the blocks to fuse in order to form lamellae. In our case, the poor crystallization conditions indeed seem to produce small blocks rather than regular lamellae. It is also to be noted that the morphology of the spherulites observed here is not conventional. Spherulites appear not as discs but rather as sectors, indicating that crystallization develops only in one direction. The same kind of observation was only reported before by Ivanov et al. [19] and Ivanov and Jonas [20] for a blend of PEEK and PEI which was also crystallized from the glassy state at a temperature just a few degrees above T_g.

Spherulites appeared as regions of lower friction. The friction contrast may be influenced by several factors: chemical composition and related adhesiveness, mechanical properties and contact area. In our case, XPS analysis (results not shown) did not reveal any differences between the chemical compositions of the two phases and no impurities were detected. PET is a non-branched polymer with a frozen conformation due to aromatic cycles. There is thus no possibility of preferential orientation or organization that would create chemical differentiation near the surface during crystallization. The lower friction might be attributed to a lower indentation of the tip into the spherulites, which are stiffer than the amorphous matrix. Moreover, due to their lamellar nature, spherulites are rougher than the amorphous phase. Since the size of the tip is large compared to the roughness of the spherulite, the contact area is lower between the spherulite and the probe than between the amorphous matrix and the probe; this may explain the lower friction observed on the spherulites. Annealing of PET films deposited on smooth glass cover-slips thus provides heterogeneous polymer surfaces presenting a controlled ratio between amorphous material and spherulites, with a contrast in terms of stiffness, roughness and swelling by organic solvents.

5. Conclusion

It has been demonstrated that PET films solvent-casted on glass cover-slips and annealed at 85 °C start to crystallize at the surface. Spherulites crop out at the surface and are subject to direct contact with the AFM tip. This process allows the production of heterogeneous polymer surfaces with a controlled ratio between semi-crystalline and amorphous phases, while keeping the same bulk properties.

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