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An atomic force microscopy study of polyester surfaces

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The surface properties of amorphous and crystalline polyester films, well below their glass transition temperature, have been studied with an atomic force microscope. For amorphous films a corrugated pattern develops on the surface as a result of scanning and the corrugations are always perpendicular to the scan direction. When scanning is stopped the pattern shows a slight relaxation; however, the surface is plastically deformed. When crystalline films are scanned, similar patterns are seen which are less pronounced and require a much longer scan time. These results suggest that the physical properties of a glassy polyester surface may be different from the bulk, and the freedom of macromolecules is reduced upon crystallization, thus suppressing molecular motion at the surface.

1. Introduction

The atomic force microscope (AFM) has been used to probe the surface structure of polymers [1–6]. Images of the surface are obtained by monitoring the deflection of a cantilevered tip as it moves across the surface under a constant applied force. The spring constant of the cantilever is known accurately and as a result, the loading force of the tip on the surface can be easily controlled. Using this technique, one can achieve high-resolution images and study surface properties on a nanometric scale.

The AFM images actually reflect the interaction between the tip and the surface. Leung and Goh [1] were the first to study the interaction between an AFM tip and the surface of amorphous polystyrene (PS). They observed the creation of a periodic pattern with nanometric dimensions as a result of scanning. Meyers *et al.* [2] studied the same material but of different molecular weight. They concluded that the PS surface is not glassy but rubber-like. Even by using an AFM in the non-contact mode, Yang *et al.* [3] found that the scanning process created bumps on amorphous PS films.

In this paper we report, for the first time, the effect of scanning both amorphous glassy and crystalline polyester films with an AFM. Polyester was chosen because films of this material are known to crystallize upon annealing at 150 °C [7], and the glass transition temperature of polyester is about 70 °C ([7] p. IV/234). As these temperatures are well above room temperature, surface melting is not expected, and the surface properties of both amorphous and crystalline polyester can be compared under similar conditions.

2. Experimental procedure

High-purity polyester samples were dissolved in a 1 : 1 solution of 2% trifluoroacetic acid and CH_2Cl_2. The films were spun-cast on freshly cleaved ruby mica by dropping the solution from a glass pipette on to the substrate. The thickness of films was estimated to be of the order of 1 μm. To obtain films in the crystalline state, samples were annealed at 150 °C for 1.5 h in a nitrogen atmosphere.

The AFM used is a Nanoscope II [8], and the tips are made of Si_3N_4 which have a radius of 20 nm with an aspect ratio of 3:1 and a spring constant of $0.58\ N\,m^{-1}$. As the tip scans the surface, a laser beam reflected from the back of the tip provides a feedback loop which adjusts the height of the sample in order to maintain a constant cantilever deflection. The images thus obtained were maps of sample displacement required to keep a constant tip-force on the surface. The operating force can be calculated from a plot of cantilever deflection versus sample displacement. The microscope can be operated in either an attractive or repulsive force mode. Unless otherwise stated, a repulsive force of 2.5×10^{-8} N was used while scanning the surfaces, and all images were obtained under ambient conditions without any filtering. Details of the operation of an AFM are provided elsewhere [8–10].

3. Results and discussion

For amorphous polyester films, oriented patterns were always created as a result of scanning the AFM tip across the surface. Fig. 1 shows the time evolution of a pattern created by continuous scanning. The scan

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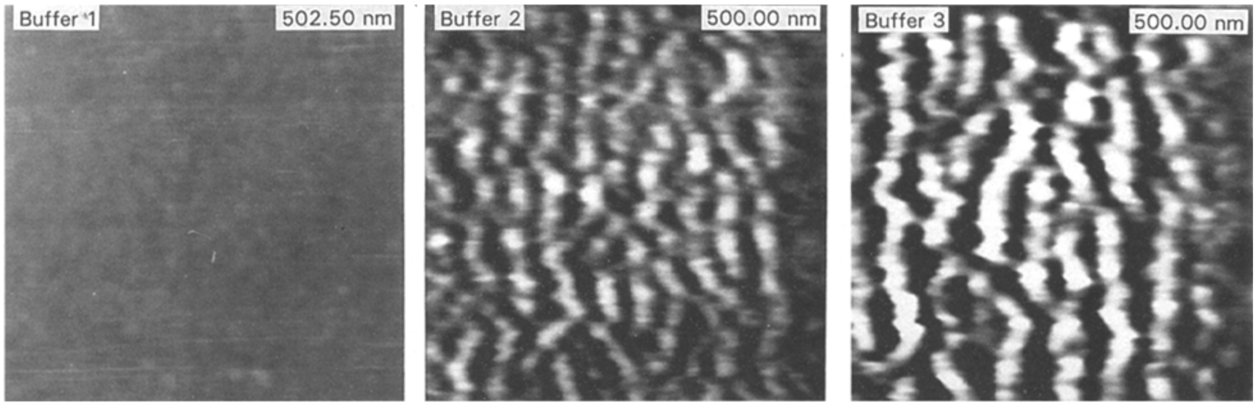

Figure 1 AFM images of an amorphous polyester surface showing corrugated patterns created by the scanning.

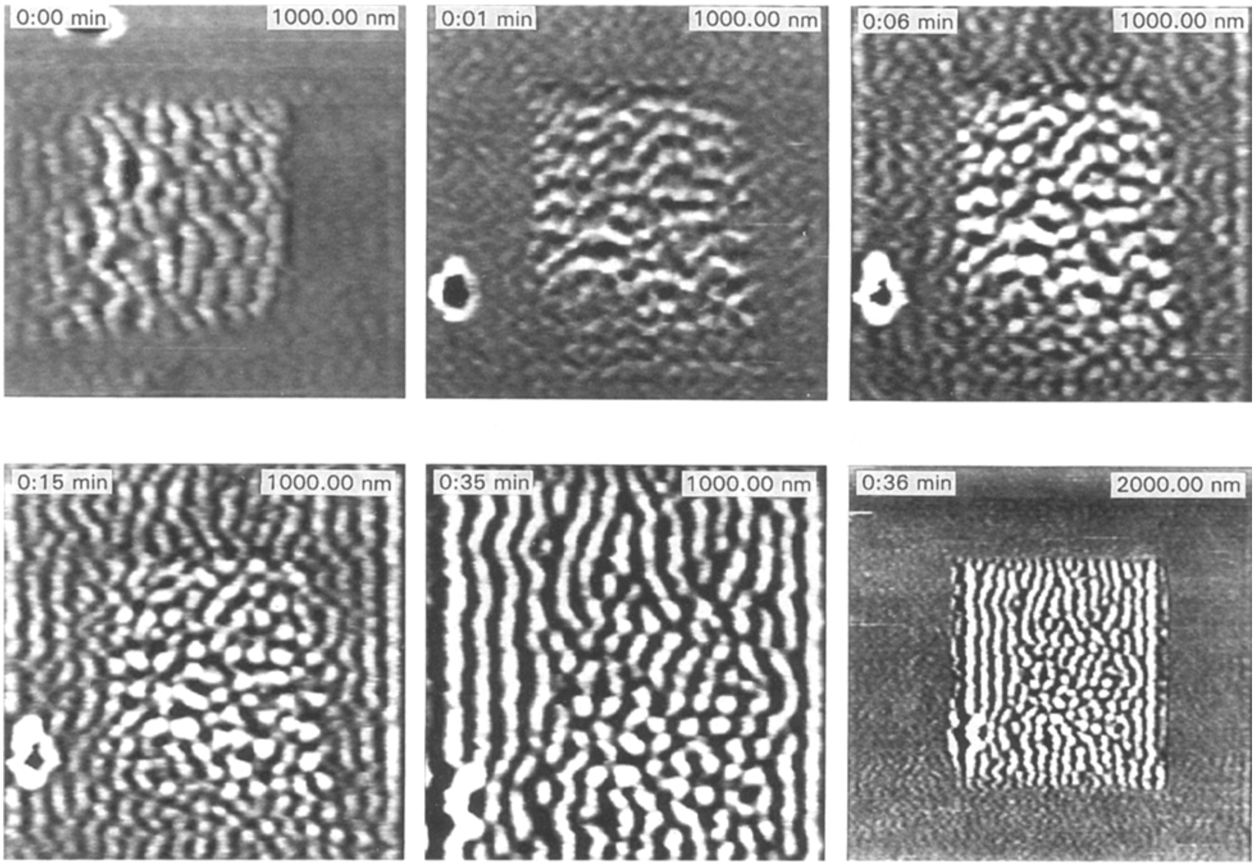

Figure 2 Sequential images of AFM showing the created patterns are always perpendicular to the scanning direction.

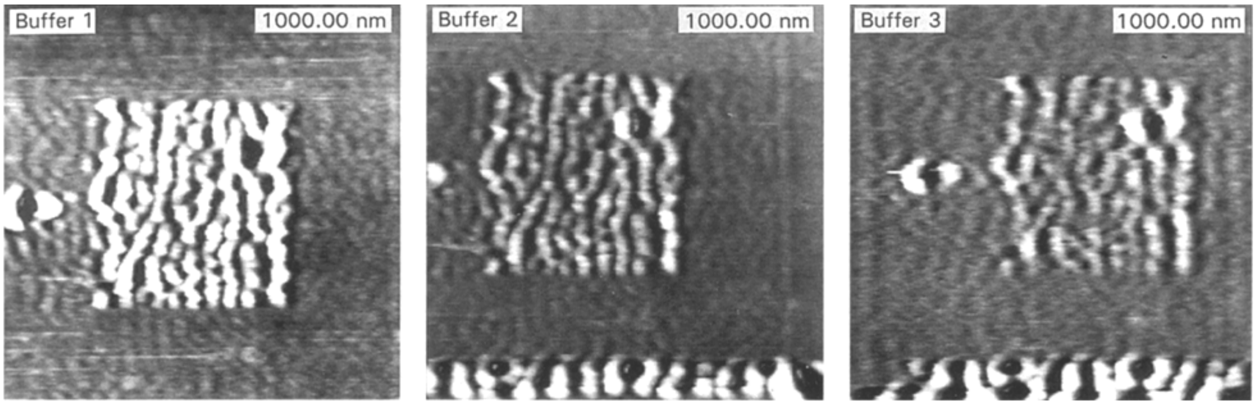

Figure 3 AFM images of an amorphous polyester surface showing pattern relaxation after scanning is stopped.

direction in all the images is from left-to-right. The image obtained on the first scan shows a smooth and homogeneous surface (see Fig. 1a). With continued scanning of the same area, surface roughness increases and a distinct pattern of corrugation develops (Fig. 1b). The ridges and valleys formed increase in vertical height and width upon further scanning, and the ridges are always perpendicular to the scan direction. Fig. 1c is an image taken after 15 min of scanning. The ridge-to-valley height in this image is 4.26 ± 2.6 nm, and the spatial period is 45.5 ± 3.7 nm.

TABLE I. Deformation height and spatial period as a function of time

Relaxation time (min)	Vertical height (± 3.2 nm)	Spatial period (± 2.8 nm)
0	9.78	62.8
25	8.12	65.7
33	6.66	70.4
125	5.22	70.4
1320	5.22	70.4

To check the effect of scanning further, another sequence of experiments was done as follows: first, a 500 nm × 500 nm area was scanned for 15 min, as before, then the area was enlarged to 1000 nm × 1000 nm and an image obtained which showed the smaller scanned area inside the larger area (Fig. 2a), and finally, the direction of scanning was rotated by 90° and scanning of the 1000 nm × 1000 nm area continued for another 20 min.

Fig. 2 shows the sequence of images thus obtained. The time in minutes, commencing with the first large-area scan before rotation, is shown at the upper left of each image. The first image shows that the pattern exists only in the previously scanned area. The crater at the top of the first image, and at the left of subsequent images, results from the initial adjustment of the force between the tip and the surface. With continued scanning of the larger area, the previously created pattern rearranges and a new pattern, again

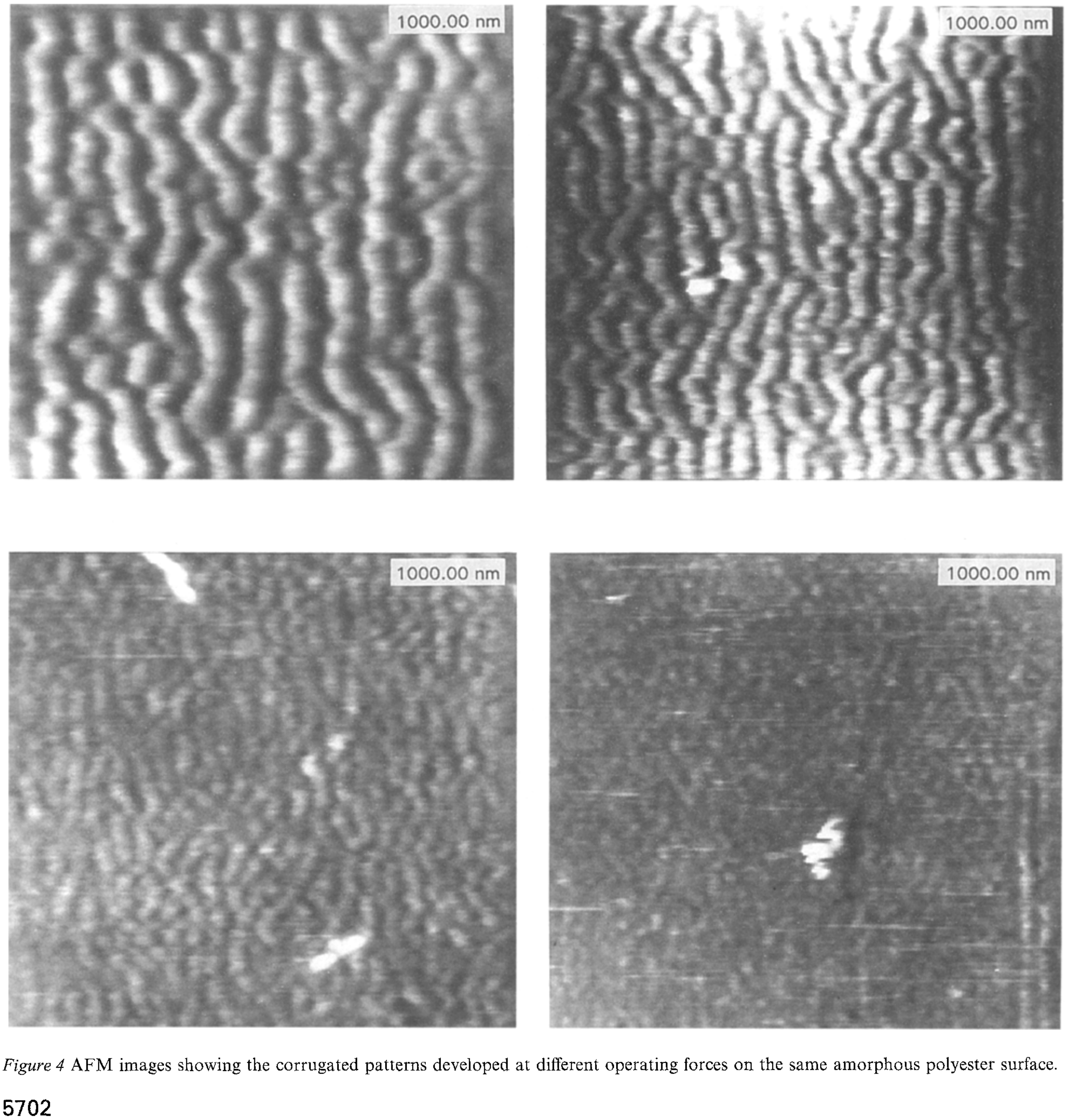

Figure 4 AFM images showing the corrugated patterns developed at different operating forces on the same amorphous polyester surface.

oriented perpendicular to the new scanning direction, started to appear. After scanning for 35 min, only faint traces of the original pattern are seen. Upon increasing the scan area to 2000 nm × 2000 nm, the pattern is again found to exist only in the scanned area. (see the last image of Fig. 2)

It is apparent that the oriented pattern is generated by rubbing the AFM tip on the surface. To determine if the surface deformation is elastic or plastic, another sequence of images was taken, and is shown in Fig. 3. Again a 500 nm × 500 nm area was scanned for 30 min, then the scan area was increased to 1000 nm × 1000 nm and the image obtained is shown in Fig. 3a. The ridge-to-valley height is 9.78 ± 3.2 nm, and the spatial period is 62.8 ± 2.8 nm. Fig. 3b and c are images taken 25 and 125 min after the image in Fig. 3a, respectively. Relaxation of the patterns is apparent. The differences in roughness between the background of these images are due to the one scan needed to obtain Fig. 3b and c. After subtracting this effect, the values of the ridge-to-valley height and the spatial period are obtained, which are listed in Table I. As time increases, the vertical height decreases, and the spatial period increases. Within the limits of accuracy, no further relaxation is seen after an additional 20 h. This result suggests that the pattern formed on the polyester surface is most likely due to elasto-plastic processes.

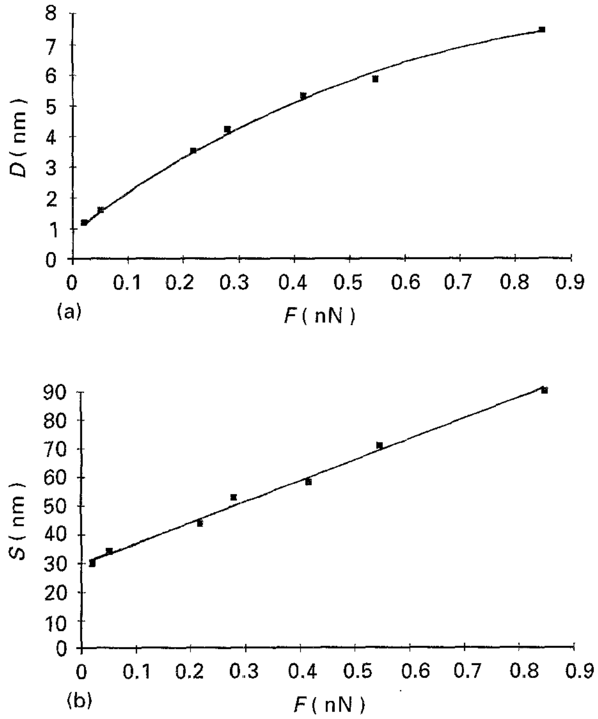

Figure 5 (a) Ridge-to-valley height as a function of operating force. (b) Average spatial period as a function of operating force.

The patterns at the bottom of Fig. 3b and c are created during the wait period between images. The tip was simply moved to the bottom of the scan area and allowed to continuously scan the same line during this period. The slight change in position of the original scan area in Fig. 3b and c is a result of slight lateral drift of the surface relative to the tip during the wait period. The repulsive force between the tip and surface was checked, and, when necessary, adjustments made before obtaining the images for Fig. 3b and c.

The deformation height and the periodic width of the pattern directly depend on the operating force. Fig. 4 shows a group of images taken under different forces on the same sample. The degree of deformation is clearly seen to be different for each. The smaller force corresponds to a lower degree of deformation and a smaller periodic width.

Graphs of the surface deformation and spatial period as a function of contact force are shown in Fig. 5. A least-square fit of these data shows that the deformation height, D, is proportional to the square root of the operating force, F, while the spatial period, S, is approximately linearly related to the force, F.

Fig. 6a is a large-area image showing the surface topography of a polyester film that was annealed at 150 °C for 1.5 h. The annealed surface appears

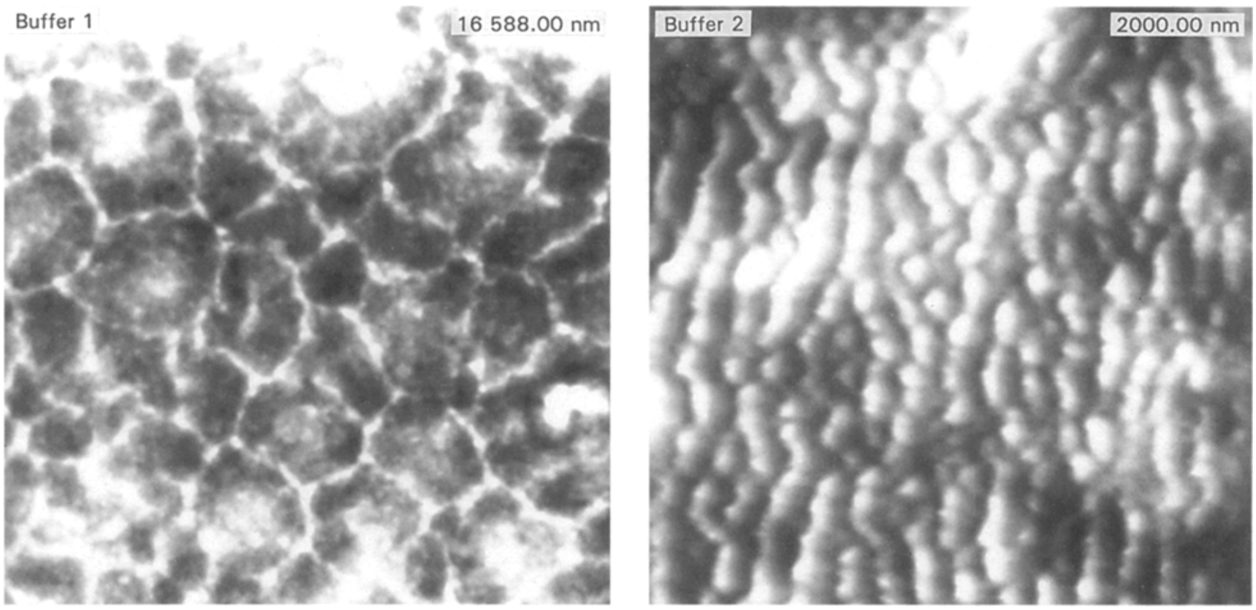

Figure 6 Surface structures of crystalline polyester films: (a) first scan, (b) after 1.5 h scanning.

segregated into domains roughly 2–2.5 μm across. The repulsive force between the tip and surface was set the same as for the previous images, and a 2000 nm × 2000 nm area was scanned for 1.5 h to obtain Fig. 6b. The pattern developed is similar to that obtained on amorphous films but the corrugations are not as continuous. The ridge-to-valley height is 10.75 ± 3.7 nm, and the spatial period is 142 ± 6.8 nm. The surface pattern was periodically checked for 2 h and no relaxation was observed, suggesting that the surface of crystallized polyester films undergoes primarily plastic deformation.

Because the glass transition temperature of polyester is about 70 °C, bulk polyester should have glass-like behaviour at room temperature. The patterns created by the interaction of the AFM tip and the surface indicates that the properties of the surface are different from the bulk, i.e. it can undergo plastic deformation. The surface of a crystallized sample is less deformable than an amorphous one. This result suggests that the formation of crystallites during the annealing process greatly reduces the freedom of macromolecules, thus increasing the rigidity of the surface.

4. Conclusions

An AFM study shows that oriented patterns are created due to the interaction of AFM tip with the surface, and the patterns are always perpendicular to the direction of scanning. The patterns are found to depend on the operating force. Because the pattern is permanent, the surface of polyester films undergoes plastic yielding. For annealed samples, the surface shows a higher degree of rigidity, which may be attributed to the formation of crystallites during annealing, and, correspondingly, to the reduction of the freedom of macromolecules. These results suggest that the surface properties of polyester are different from its bulk.

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