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PHYSICAL CHEMISTRY

A New Type of Surface Structuring Accompanying the Rolling of Glassy Poly(ethylene terephthalate)

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A popular type of inelastic deformation of glassy and crystalline polymers is rolling [1]. At the same time, the mechanism of structural rearrangements accompanying the rolling of polymers has been studied and understood much less than in the case of other, more frequently used types of inelastic deformation, such as uniaxial tension and uniaxial compression. Rolling underlies a popular technological method by which a polymer film is continuously pulled between two rollers rotating in opposite directions.

Such a treatment leads to molecular orientation of polymers [2], and also to other significant structural rearrangements [3]. By such a treatment, the mechanical and strength properties of polymer can be optimized.

Importantly, most studies of the structural rearrangements accompanying the rolling of polymers were performed on crystalline polymers with a two-phase structure. In this case, X-ray powder diffraction analysis, electron microscopy, and other methods based on phase contrast can be efficiently used. For this reason, investigations of the structural rearrangements in the course of the rolling of amorphous polymers are much fewer. Nonetheless, there are quite a lot of studies of the effect of rolling on the deformation and strength properties of amorphous glassy polymers [4]. These studies showed that rolling of polymers can be considered as a sort of modifying influence on a polymer that can be used for optimizing its mechanical properties.

Previously [5–9], we described a procedure for visualizing and characterizing the structural rearrangements accompanying polymer deformations of various types (uniaxial tension, uniaxial compression, rolling, etc.). This procedure is quite simple and consists in applying a thin (nanosized) metal coating to the polymer surface. The subsequent deformation (shrinkage) of the polymer leads to structuring of a special kind on the polymer surface. The structures forming thereat contain information on the structural rearrangements of the polymer substrate.

In particular, this procedure was used for investigating the thermally stimulated shrinkage of amorphous polycarbonate subjected to rolling in the glassy state [10]. It was shown that the polycarbonate subjected to deformation of this kind, in contrast loadings of other types (tension and compression), demonstrates a complex pattern of surface structuring. It turned out that the rolled polymer contains quote extensive discrete zones in which the polymer is oriented in various directions. The detected structural features of the amorphous polymer deformed under the rolling conditions have not yet been adequately explained.

In this work, we made a direct microscopic study of the structural rearrangements accompanying the rolling of another amorphous polymer, polyethylene

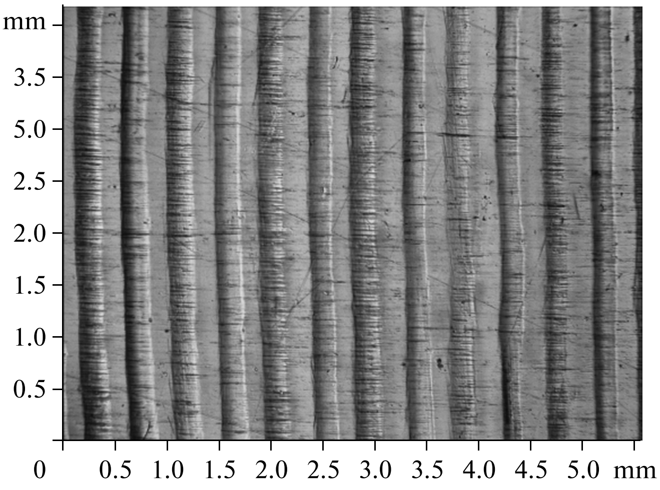

Fig. 1. Light micrograph of a PET sample rolled by 6%. The rolling direction is horizontal.

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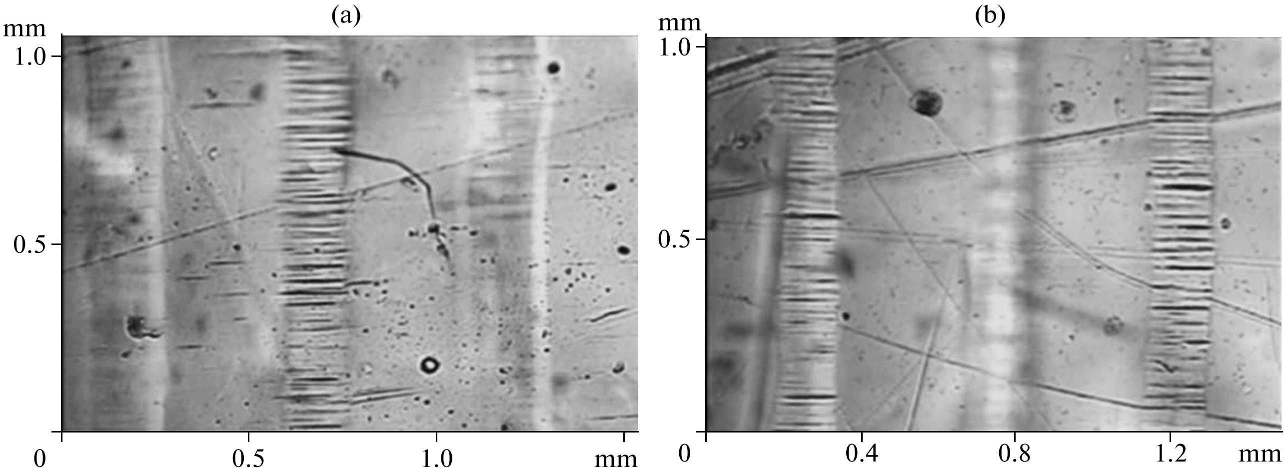

Fig. 2. Light micrographs of a fragment of the PET sample shown in Fig. 1 at higher magnification with focusing on (a) one of the sides of the film and (b) the other side. The rolling direction is horizontal.

terephthalate (PET). In the study, 510-μm-thick unoriented films of amorphous PET were used. Film specimens 18 mm wide and 85 mm long were subjected to rolling on a laboratory setup between two rotating rollers at room temperature to various degrees of rolling $\lambda = 1.018–1.42$. The transparent PET specimens obtained by the rolling were examined with a VOMO MBS-9 light microscope (USSR), a CamScan-4 scanning electron microscope (Cambridge Instruments, UK), and a Nanoscope IIIa atomic-force microscope (Russia). The microscopic study data were processed by the FemtoScan Online specialized scientific software [11].

Figure 1 presents the light micrograph of a PET sample rolled by 6% at room temperature. It is well seen that such rolling gave rise to a system of regular stripes in the transparent uniform film. Such stripes are parallel to each other, normal to the rolling axis, and extend from one of the edges of the polymer film to the other. At first glance, it seems that discrete parallel ridges and grooves formed on the film surface. However, at higher magnifications, it proved that the detected pattern has a more complex structure.

It turned out that these stripes crossing the entire surface of the specimen (Fig. 1) alternate on different sides of the polymer film. If the microscope is focused on one of the film sides, only every second detected stripe is in focus (Fig. 2a). If the microscope is focused on the other film side, the remaining stripes in this fragment of the rolled film are in focus (Fig. 2b). In other words, the discovered stripy structures do not pierce the entire cross section of the polymer. These stripes are surface formations lying alternately on one or the other side of the rolled film.

One more feature of the detected structures is their unsmooth surface. In Fig. 1 and, especially, Fig. 2, it is clearly seen that the surface of the stripes is crossed by dark lines. These lines are normal to the major axis of the stripes and, therefore, aligned with the rolling direction. The structure of these formations can be identified and described in detail by scanning electron microscopy.

It is well seen that the stripes discovered with a light microscope (Figs. 1, 2) are elevations of a sort on the surface of the smooth film (Fig. 3). These elevations have folded transverse relief. The transverse folds have different heights and are located not very regularly. Their pitch (the distance between neighboring folds) ranges from 5 to 50 μm.

The atomic-force microscopy quantitatively estimated the roughness of the emerging relief. The large stripy structures rise over the surface by 0.5 μm. The liny structures coating these stripes extend to a depth of ≈200 nm. Importantly, the parameters of the

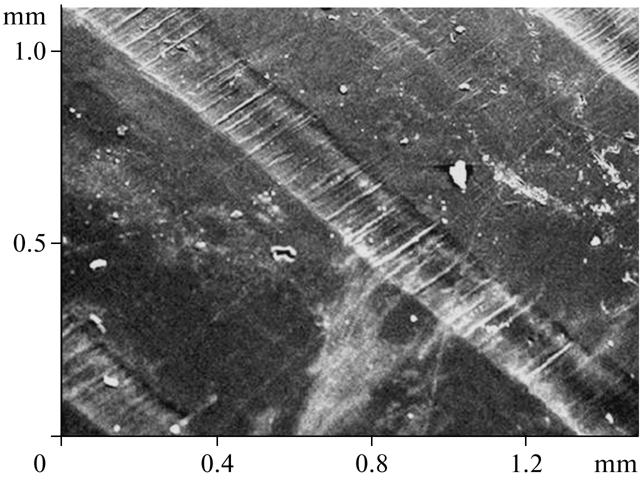

Fig. 3. Scanning electron micrograph of the surface of the PET film rolled by 6% at room temperature. The arrow indicates the rolling axis. The image was taken at an angle. The scale bar length is 100 μm.

microrelief described above for the first time depend on the deformation conditions (rolling characteristics, the thickness and nature of the film, etc.).

Thus, by the direct microscopic study, we detected and described a previously unknown type of surface structuring occurring in the rolling of an amorphous glassy polymer. The mechanism of the discovered phenomenon is being explored.

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