

Evaluation of the Deformation Strength Properties of a Fluorinated Polymer Layer on the Surface of Poly(ethylene Terephthalate) Films

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Chemical surface modification of materials and articles is a promising technique of modern polymer chemistry and technology. Conceptually, such an approach involves the chemical modification of polymer surface layers to impart to the material some generally new and sometimes valuable physicochemical, physicomechanical, and other properties. Many fundamental and applied aspects of polymer surface modification are currently being actively developed and were generalized and considered in detail in a recent monograph [1]. There is one more urgent problem that has not yet been solved completely until recently. This is the evaluation of the deformation strength properties of layers produced on the polymer surface by modifying treatments, such as chemical surface modification, low-temperature plasma treatment, UV treatment, etc. Such information can be critical for understanding many phenomena in polymer surface modification and for solving important applied problems. Such information is scanty, mainly, because of the absence of a general method for evaluating the deformation strength properties of thin (down to nanosized) polymer surface layers.

A new line of scientific research focusing on the structural mechanical behavior of polymer films with thin rigid coatings have recently been intensely developed [2, 3]. It was shown that deformation of such objects is accompanied by surface structuring of special sort, which gives the simplest way to create polymer films with regular microrelief. Owing to this microrelief, these objects are quite promising for producing polymer films with valuable optical properties [4].

All the specific features of the unique surface structuring were demonstrated by the example of the deformation of polymers with low-molecular-weight coat-

ing (metals, carbon, oxides, etc) [5]. Two conditions are necessary for this structuring to occur: (1) Young's modulus of the polymer film should be considerably lower than that of the material of the coating and (2) the coating thickness should be negligibly small in comparison with the polymer substrate thickness. Systems meeting these conditions were called the hard coating on yielding substrate [2, 5].

These systems can be obtained not only by applying hard coatings to polymers. It was demonstrated that such structures can be formed by chemical modification [6] or cold-plasma treatment [7] of polymer surface layer. In all these cases, a system of a relatively rigid coating and a yielding substrate emerges, and the deformation of such systems is accompanied by the said surface structuring characterized by the formation of regular reliefs. The previously [5] established relationship between the parameters of the forming microrelief and the properties of the materials of the substrate and the coating makes possible evaluating the deformation strength properties of thin, including nanosized, layers that are applied to polymer films or created within their surface layer. It is very difficult or even impossible to make this evaluation another way.

In this work, we attempted to create systems of hard coating on yielding substrate on the basis of poly(ethylene terephthalate) films subjected to surface fluorination from the gas phase [1]. Using approaches developed before [5], we evaluated the mechanical characteristics of layers forming on the polymer surface.

In the experiments, 100- μm -thick extruded poly(ethylene terephthalate) films were tested. The films were fluorinated according to a previously developed [8, 9] procedure in a stainless-steel vacuum reactor by a mixture of 15 vol % fluorine and helium at 20°C for 30, 120, and 360 min.

The ultimate strength σ^* of the fluorinated surface layer was determined as

$$L = 3h\sigma^*/\sigma_0, \quad (1)$$

where L is the length of a coating cracking fragment in the stretching axis direction, h is the coating thickness, and σ_0 is the stress in the substrate [5].

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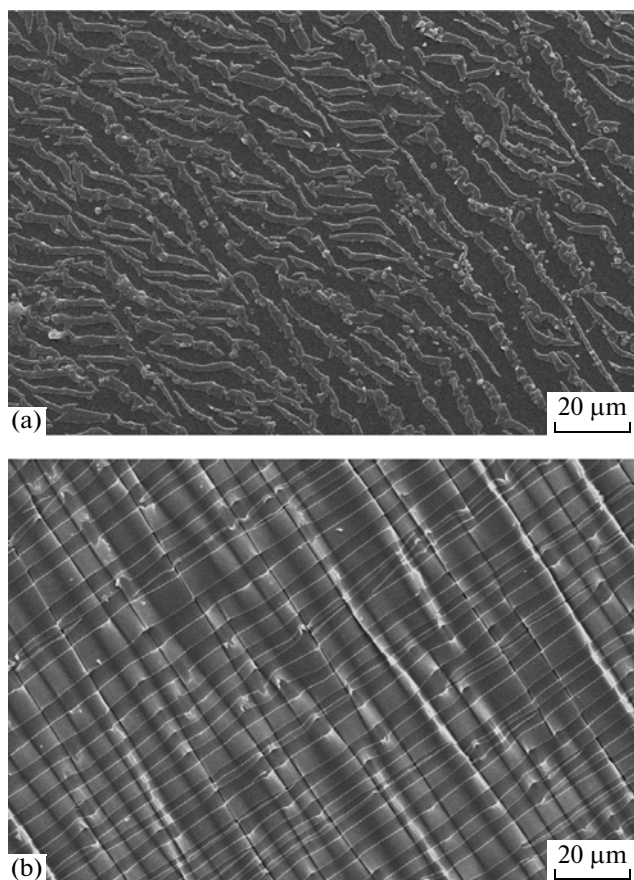


Fig. 1. Scanning electron micrographs of poly(ethylene terephthalate) film specimens that were subjected to gas-phase fluorination for 30 min and then stretched (a) at room temperature until necking began and (b) at 90°C by 100%.

The plastic strain ε of the surface layer was estimated at

$$\varepsilon = \frac{L_{\text{coat}}\lambda}{L_{\text{total}}} - 1, \quad (2)$$

where L_{coat} is the sum of the lengths of coating cracking fragments, L_{total} is the total length of the segment on which the tests were carried out, and λ is the degree of stretching of the polymer.

Figure 1 presents the scanning electron micrographs of two specimens of gas-phase fluorinated poly(ethylene terephthalate) films. The specimens were deformed at room temperature (below the glass transition temperature T_g) until necking began (Fig. 1a) and at 90°C (above the glass transition temperature T_g) by 100% (Fig. 1b). Figure 1 shows that not only does the surface fluorination of the poly(ethylene terephthalate) films result in the well-studied above-described [1] chemical modification of their surface layer, but also leads to its formation as a morphologically expressed surface structure. It is well seen that the stretching of the prefluorinated polymer films causes the surface structuring that is completely similar to

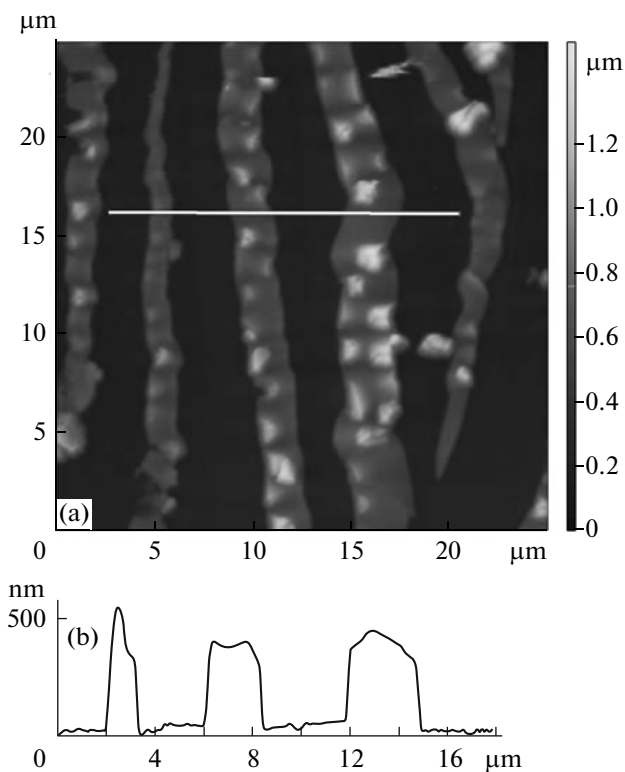


Fig. 2. (a) Atomic force microscopy image of the surface of the poly(ethylene terephthalate) specimen that was subjected to gas-phase fluorination for 30 min and then stretched at room temperature until necking began, and (b) the corresponding profilogram along the straight line shown in Fig. 2a.

that observed while deforming polymer films with thin metal coatings [5]. The polymer surface layer breaks up into fragments of approximately identical size. If the polymer substrate is deformed above T_g , a regular folded relief forms. This phenomenon is likely to be related to the fact that, on the polymer surface, a thin layer forms, consisting of a probably cross-linked polymer that has much better mechanical properties than the substrate polymer has. This result opens realistic approaches to evaluating the deformation strength properties of the modified layer produced on the polymer surface by gas-phase fluorination.

Let us estimate the strength by Eq. (1), in which all the terms, except the conditional thickness of the fluorinated polymer layer, are known. This thickness can be estimated by atomic force microscopy. Figure 2 presents the atomic force microscopy image of the surface of the poly(ethylene terephthalate) specimen that was subjected to gas-phase fluorination for 30 min and then stretched at 20°C until necking began. Figure 2 shows that, while deforming the polymer substrate, the polymer breaks up into approximately identical fragments ~450 nm thick. Such thickness correlates well with the thicknesses of surface layers of

fluorinated polymers as determined by other methods [1, 10].

Substitution of the thickness 450 nm to Eq. (1) gives that the strength of the polymer layer on the poly(ethylene terephthalate) film surface is 60.7 MPa if deformed at room temperature and 3.8 MPa if deformed at 90°C. This suggests that the fluorinated polymer layer, although chemically modified [11], “remembers” the glass transition temperature T_g of poly(ethylene terephthalate). The strength of the fluorinated surface layer is similar to that of the surface layer produced on the poly(ethylene terephthalate) film surface by cold-plasma treatment [7].

The plastic strain of the fluorinated layer on the poly(ethylene terephthalate) film surface was estimated by Eq. (2). Despite a certain data scatter, the plastic strain induced by polymer substrate deformation at room temperature is 15–30%, whereas it at 90°C is 8–10%. Thus, the long fluorination of poly(ethylene terephthalate) sharply reduces its elongation at rupture. This is likely to be related to the cross-linking and/or destruction of macromolecules in the surface layer, which complicates the polymer orientation and, consequently, reduces the elongation at rupture.

Thus, in this work, we, for the first time, evaluated the deformation strength properties of the fluorinated polymer layer on the poly(ethylene terephthalate) film surface. It was shown that not only does the fluorination change a number of physicochemical properties, but also it significantly affects such basic polymer characteristics as strength and elongation at rupture.

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