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PHYSICAL CHEMISTRY

Formation of a Regular Microrelief in Deformation of Plasma-Treated Polymer Films

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Deformation of polymer films with thin hard coatings is accompanied by spontaneous formation of a regular periodic microrelief on their surface. This phenomenon is general and is observed in all systems of hard coating on yielding substrate, regardless of their scale. In all cases where such a system can be obtained (on application of thin coatings on polymers [1, 2] or under the action of some natural processes [3]), its deformation is accompanied by spontaneous formation of a regular relief. The mechanism of this phenomenon was analyzed previously [4–6].

One of the most widely used methods for modifying the surface of polymers (and some other materials) is their treatment with cold plasma [7]. The plasma treatment of the polymer surface changes mostly the contact properties of the polymer (e.g., wetting, adhesion to thin metal layers applied by vacuum deposition and other methods, adhesion of printing inks, etc.). At the same time, the deformation-strength properties of the forming modified polymer nanolayers are as yet unknown.

In this work, we made the first attempt to evaluate the deformation-strength properties of modified surface layers produced by polymer treatment with cold plasma. It was shown that such polymer treatment gives rise to a certain surface layer that not only is well known to have a modified chemical composition affecting the above properties, but also has a regular microrelief, which uniquely indicates that polymer treatment with cold plasma produces a system of hard coating on yielding substrate.

In this work, commercial polymer films (poly(ethylene terephthalate), poly(vinyl chloride), polycarbonate, and rubbers) were treated with low-temperature plasma created by an electric discharge on an Eiko IB-3 ion coater (Japan). The treated polymer films were stretched to a necessary degree, and their surface was studied with a Hitachi S-520 scanning electron microscope (Japan) and a Nanoscope IIIa atomic force microscope (USA).

As noted above, deformation of systems of hard coating on yielding substrate gives rise to a regular microrelief. Figure 1 gives a typical example of such surface structure formation. It is well seen that deformation causes a metal coating on the surface of a polymer film to break up into a set of regularly located islands of approximately identical size and a regular wavy relief simultaneously emerges in the coating. The main structural features of systems of hard coating on yielding substrate are that the coating thickness must be negligibly small in comparison with the substrate thickness and that the modulus of elasticity of the coating must be several orders of magnitude higher than that of

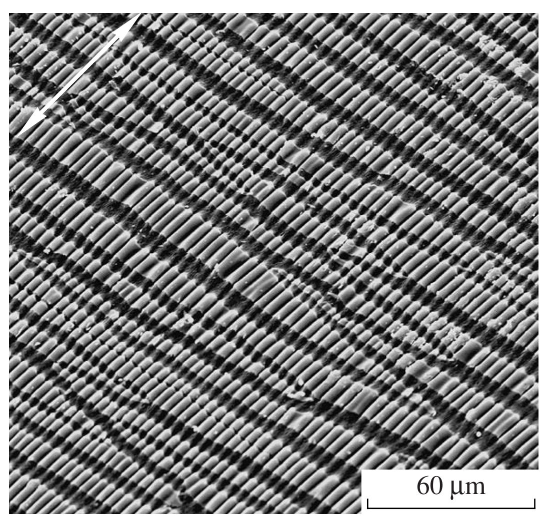

Fig. 1. Scanning electron photomicrograph of a poly(vinyl chloride) sample with a thin (21 nm) platinum coating after stretching the sample by 50% at a rate of 1 mm/min at 90°C. The arrow shows the stretching direction.

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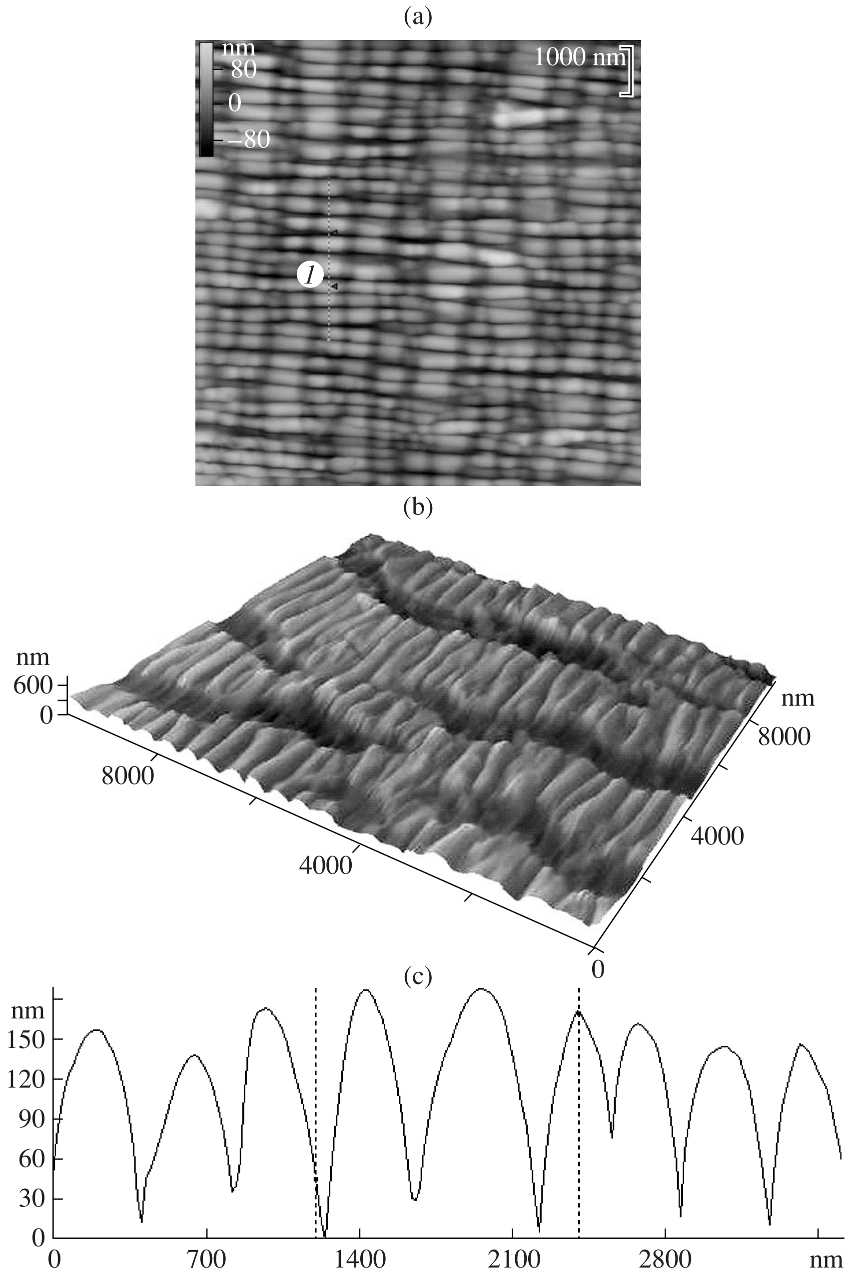

Fig. 2. (a) Atomic-force photomicrograph of a poly(ethylene terephthalate) sample treated with plasma for 1 min and then stretched by 50% at 90°C, (b) its three-dimensional reconstruction, and (c) the profilogram of region *1* in panel (a).

the base. It is these structural features of systems of hard coating on yielding substrate that determine the above phenomenon, the mechanism of which was explained in detail earlier [4–6].

Let us now consider consequences of polymer surface pretreatment with cold plasma. Figure 2 shows that plasma treatment of polymer films leads not only to chemical modification of their surface layer, but also to structuring that is completely similar to that caused by deformation of polymer films with a thin metal coating (compare Figs. 1 and 2a). The polymer surface layer breaks up into fragments of approximately identical size, and a regular wavy relief emerges.

This phenomenon is likely to be related to the fact that, on the polymer film surface, a thin layer of presumably cross-linked polymer forms, which has much better mechanical parameters than the material of the polymer base. As a result, the situation is similar to that observed in coating the polymer surface with thin layers (coatings) of material by ion plasma and/or thermal deposition. In other words, this system is a system of hard coating on yielding substrate. Subsequent deformation of polymer films subjected to plasma surface treatment leads to spontaneous formation of a micron-scale regular microrelief on their surface, with the parameters of this microrelief being dependent on the mechanical properties of the polymer and the coating, the film stretching conditions, and the duration and intensity of plasma treatment of the polymer surface. Note that the detected phenomenon is general since it is observed in deformation of other plasma-treated polymers (polyvinyl chloride, plasticized polyvinyl chloride, polycarbonate, and some rubbers).

The obtained result for the first time opens real approaches to evaluating such important parameters as the deformation-strength properties and thickness of the modified layer forming on the polymer surface under various conditions of cold plasma treatment.

The detected phenomenon has an undoubted practical aspect. The fact is that production of polymer films with a regular microrelief allows one to solve a number of important issues. In particular, such films can be used as elements of optoelectronic devices and information display systems, e.g., liquid-crystal displays, which contain one or several transparent films with a regular microrelief for controlling light fluxes. Production of a micron-scale surface microrelief on polymer films is currently complex and expensive. Methods for producing it have been recently reviewed [8].

Using deformation of polymer films with thin coatings for creating a regular microrelief, which imparts them with valuable optical properties, is quite promising [9]. However, this approach has one significant drawback. The fact that, after producing a regular microrelief on a polymer (Fig. 1), the applied coating should be removed from its surface. This is usually performed by dissolving the coating in specially selected solvents, as a rule, such aggressive liquids as concentrated acids and alkalis. Using these substances in creating transparent polymer films with a regular microrelief results in the formation of a large amount of aggressive liquid components (solutions of metal compounds and other substances), which must be disposed. This significantly increases the cost and complexity of the entire process of production of a transparent polymer film with a regular microrelief.

The possibility of producing a regular microrelief on polymer films by treating them with cold plasma is promising for creating a new "dry" method for obtaining new types of polymer films with valuable optical properties in a much simpler way at much lower cost.

REFERENCES

1. Volynskii, A.L., Chernov, I.V., and Bakeev, N.F., *Dokl. Phys. Chem.*, 1997, vol. 355, nos. 4–6, pp. 247–249 [*Dokl. Akad. Nauk*, 1997, vol. 355, no. 4, p. 491].
2. Volynskii, A.L., Bazhenov, S.L., Lebedeva, O.V., Yaminskii, I.V., Ozerin, A.N., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A*, 1997, vol. 39, no. 11, p. 1805.
3. Volynskii, A.L. and Bazhenov, S.L., *Eur. Phys. J., Soft Matter*, 2007, vol. 24, no. 4, p. 317.
4. Volynskii, A.L., Bazhenov, S.L, and Bakeev, N.F., *Ros. Khim. Zh. (ZhVKhO Im. D.I. Mendeleeva)*, 1998, vol. 42, no. 3, p. 57.
5. Volynskii, A.L., Bazhenov, S.L., Lebedeva, O.V., and Bakeev, N.F., *J. Mater. Sci.*, 2000, vol. 35, p. 547.
6. Volynskii, A.L., Bazhenov, S.L., Lebedeva, O.V., Ozerin, A.N., and Bakeev, N.F., *J. Appl. Polym. Sci.*, 1999, vol. 72, p. 1267.
7. Rybkin, V.V., *Soros. Obrazovat. Zh.*, 2000, vol. 6, no. 3, p. 58.
8. Belyaev, V.V., *Opt. Zh.*, 2005, vol. 72, no. 9, p. 79.
9. RF Patent 2 319 556, Application 2006110811, 2006.