

On the Effect of the Nature and Physical State of a Polymer Support on the Stress–Strain Characteristics of Metallic Coatings¹

A. L. Volynskii^a, D. A. Panchuk^a, S. V. Moiseeva^c, S. S. Abramchuk^a,
O. V. Lebedeva^b, L. M. Yarysheva^a, N. F. Bakeev^b

^a Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia

^b Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences,
Profsoyuznaya ul. 70, Moscow, 117393 Russia

^c Moscow State Pedagogical University, Nesvizhskii per. 3, Moscow, 119882 Russia
e-mail: volynskii@mail.ru

Received December 25, 2007;

Revised Manuscript Received June 05, 2008

Abstract—A newly proposed microscopic procedure makes it possible to estimate the strength of thin (nanometric) coatings deposited onto various polymer supports. The strength of the deposited coating is shown to increase dramatically when the thickness of the coating decreases below 15 nm. It was also found that the strength of the coatings is controlled by the physical state of the polymer support. The Interfacial layer formed at the early stages of metal deposition onto the polymer surface is characterized by a higher strength as compared with that of a pure metal deposited onto the above interfacial layer. This observation can be explained by the following reasons: first, the dimensions of metallic grains in the interfacial layer are much smaller than those in a pure metal and, second, the intergrain space in the interfacial layer is filled with polymer matrix. At the same time, both the temperature and the adsorptionally active liquid medium affect polymer partitions in the interfacial composite layer and thus control the overall strength of thin coatings (≤ 15 nm). In the case of thicker coatings, the strength of the coating gradually decreases independently of the nature and state of the supporting polymer and approaches the strength of the bulk metal.

DOI: 10.1134/S0965545X09030092

INTRODUCTION

Polymeric films with thin metallic coatings are widely used, for example, in microelectronics, computing technology, and the packaging industry. However, there exist several problems, and their solution is crucial for the development of this scientific direction. One challenging problem is the specific features of the structure of the interfacial layer formed between a coating and a polymer support, which strongly affects interfacial adhesion. This problem has been described in [1, 2], where PET–silicone oxide systems were investigated. A layer of silicone oxide deposited onto a polymer surface presents a barrier to oxygen penetration through the polymer film; hence, this system can be used in practice as a packaging material in the pharmaceutical and food industries [3].

Usually, the thickness of coatings deposited onto polymeric films ranges from several to tens of nanometers. As is known [4–6], on passage from the micro- to the nanoscale, the physical, mechanical, physicochemical, and other characteristics of materials qualitatively change. In this connection, the development

of new methods for gaining reliable information on the characteristics of nanomaterials seems particularly important.

However, nowadays, there is no reliable information on the stress–strain characteristics of a material with dimensions ranging from several to tens of nanometers. Indeed, one can hardly imagine the use of traditional testing methods for solids whose geometric sizes are tens to hundreds of angstroms. Fundamental information on the mechanical characteristics of nanomaterials can be primarily gained by using indentation testing methods [7–9]. This approach has certain obvious drawbacks; for example, these methods do not allow an adequate estimation of such important characteristics of solids as the Young's modulus, elongation at break, or strength.

In this connection, the results of our recent studies on estimating the stress–strain characteristics of nanometric coatings deposited onto polymer films seems very important. This estimation is based on the correlation [10–13] between the parameters of a surface microrelief induced upon deformation of coated polymer films and the characteristics of both the coating and polymer support. Even in the pioneering works that used the above approach, the mechanical characteristics of the metallic coatings, such as strength and

¹ This work was supported by the Russian Foundation for Basic Research, project nos. 05-03-32538 and 06-03-32452, and a State Grant in Support of Leading Scientific Schools, NSh-4897.2006.

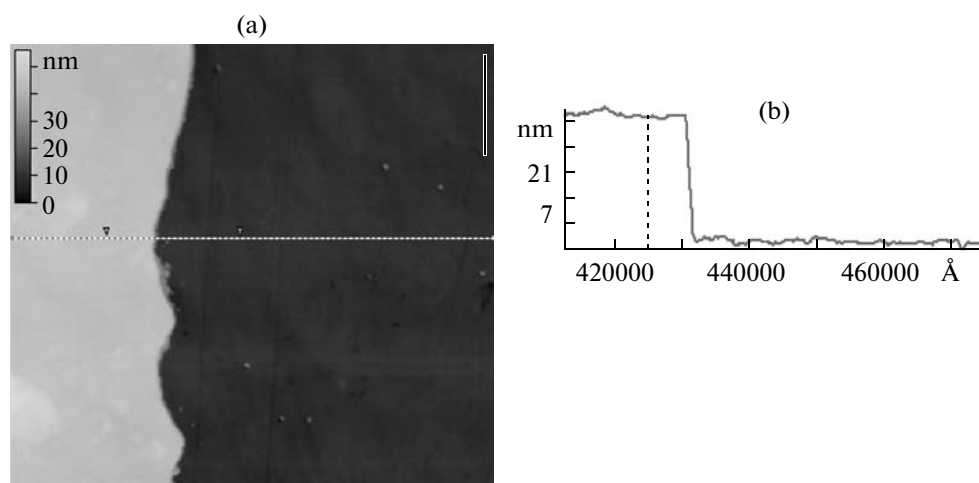


Fig. 1. (a) AFM image of a scratch in the gold-based coating deposited onto a glass support by the method of ionic plasma deposition and (b) the corresponding profilogram.

plasticity, were shown to increase considerably when the dimensions of phases go down below 30 nm and this unequivocally proves the ideas concerning a unique state of solids in nanoscale layers [14].

The objective of this work is the possible effect of the nature and physical state of polymer support on stress–strain characteristics of nanometric coatings.

EXPERIMENTAL

In this work, we used commercial films of unoriented PET with a thickness of 100 μm and PET films after their annealing for 2 h at 140°C; we also studied PVC and PVC films containing 15% dioctyl phthalate (DOP). The test samples were cut from the films as dumbbell-shaped specimens with a gage size of 6 \times 20 mm; then, the samples were decorated with thin gold or platinum layers of different thicknesses by ionic plasma deposition on a Eiko IB-3 setup. Tensile drawing of the samples was performed both in air and in the presence of adsorptionally active liquid environments on an Instron 1122 universal tensile machine.

For the purposes of this work, it was especially important to correctly estimate the thickness of the metallic coating deposited onto the polymer film. This estimation method is based on the calibration plot relating the thickness of the coating thickness to time of deposition under standard conditions. To this end, glass plates were decorated with gold or platinum layers by ionic plasma deposition, and the thickness of the coating was changed by varying the time of deposition. Then, the deposited layer was scratched with a pointed wooden stick, and this scratch was examined by atomic force microscopy on a Nanoscope-2 AFM setup (Digital Instruments, Santa Barbara, United States) in the regime of contact forces. We emphasize that pay similar procedure of metal deposition onto a polymer support failed to provide any adequate esti-

mates because the polymer surface appeared to be too soft and the pointed wooden stick scratches it more deeply, thus confusing the results of the estimation procedure.

Figure 1 presents the typical results of such measurements. In the left-hand part of the AFM image, the light region corresponds to the gold layer, whereas the dark region in the right-hand part of the image shows the glass surface. This scratch in the coating is easily detected by the atomic force microscope (Fig. 1a), and the corresponding surface profilogram (Fig. 1b) makes it possible to estimate the coating thickness with high accuracy. In this way, the calibration curve in the (coating thickness)–(deposition time) coordinates was plotted; later, this plot was used for the controlled deposition of gold or platinum layers with the required thickness onto PET films. Figure 2 presents the calibration curve plotting the thickness of the metallic coating deposited onto a glass surface against the time of deposition.

Specific features of surface structuring induced by tensile drawing of polymer films with thin metallic coatings were examined on a Hitachi S-520 scanning electron microscope. The numerical values of the mean dimensions of the fractured fragments of the coating were estimated from the corresponding SEM images using the Femtoscan Online software package [15]. The structure of the interfacial polymer–metal layers was studied on a LEO 912AB transmission electron microscope with an OMEGA filter; for TEM studies, the test samples were cut into ultrathin 100-nm sections with a diamond knife on a Reichert–Jung ultramicrotome. The samples were thin-sectioned at an angle of 30°–45° to the plane of the film surface (coating), and this geometry made it possible to study the fine structure of the deposited metallic layer.

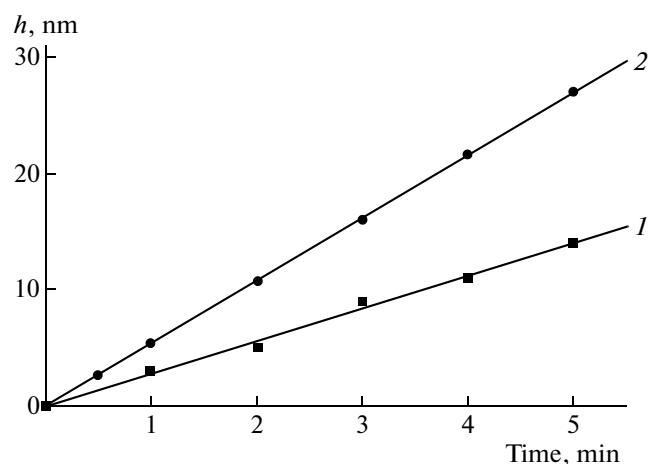


Fig. 2. Thickness of (1) gold-based and (2) platinum-based coatings h vs. duration of ionic plasma deposition onto a glass surface.

The development of a new method for estimating the stress–strain characteristics of thin (nanometric) metallic coatings was based on the earlier results of studying the structural mechanical response of polymer films with a surface-deposited thin rigid coating [10–13]. In these works, the surface of polymer films with thin rigid coatings after their deformation under conditions of uniaxial tensile drawing has been examined by direct electron microscopic observations. Figure 3 presents an SEM image illustrating the surface relief of a PVC film with a deposited thin (10 nm) platinum coating after its tensile drawing by 100% at 90°C. As is well seen, fracture of the coating on the surface of polymer support is accompanied by the development of a system of fractured fragments (light-colored bands) with quite uniform dimensions. In this work, it seems expedient to discuss in brief the mechanism of

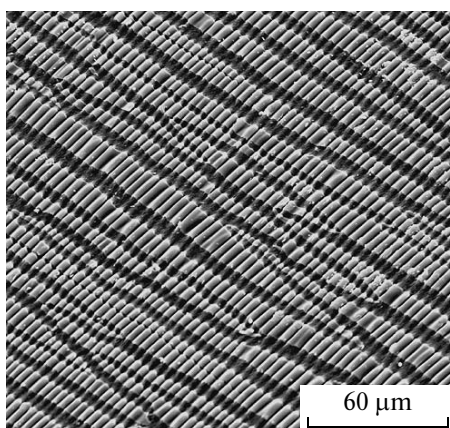


Fig. 3. SEM image of the PVC sample with a thin (10 nm) platinum-based coating after its tensile drawing by 100% at 90°C with a strain rate of 1 mm/min; $\times 500$.

regular fragmentation of the coating in the course of tensile drawing of the polymer support.

Regular fragmentation of a rigid shell is the result of specific features of the mechanical stress transfer from a compliant (soft) support to a solid (rigid) coating through an interfacial boundary. Independently of the mode by which a soft polymer support is deformed (either uniform or inhomogeneous via necking), mean size L of the fractured fragments along the direction of tensile drawing appears equal to [12, 16, 17]

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

where h is the thickness of the coating, σ^* is the breaking strength, and σ_0 is the acting stress in the polymer support.

Therefore, deformation of a polymer with a thin rigid coating allows one to establish the correlation between the most important property of solids, their strength upon tensile drawing, and the mean dimensions L of fractured fragments induced during the deformation of the above systems. The dimensions of the fractured fragments can be easily assessed in direct microscopic experiments. Obviously, in meaning, the established correlation serves as the basis for a simple and direct method allowing estimation of the stress–strain characteristics of coatings with different thicknesses (including nanometric scale) deposited onto polymer supports.

RESULTS AND DISCUSSION

Figure 4 presents the strength of platinum and gold calculated by means of Eq. (1) plotted against the thickness of a metallic layer deposited onto the PET film. As follows from Fig. 4, it appears that the strength of both metals is almost completely independent of the thickness when the latter parameter ranges from 30 to ~ 15 nm. In this case, the strength of gold varies from

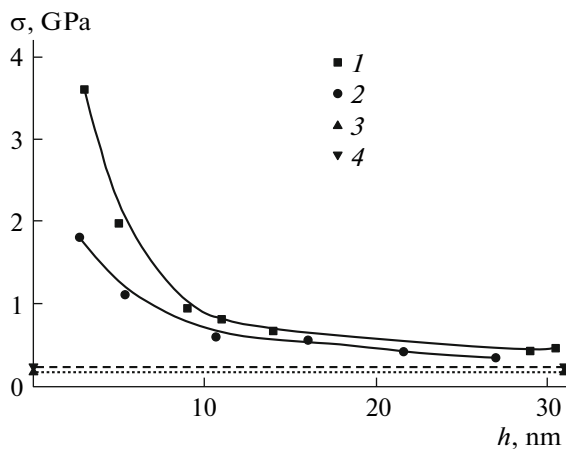


Fig. 4. Strength of (1) gold-based and (2) platinum-based coating vs. thickness upon deformation of PET samples at 20°C with a strain rate of 0.2 mm/min; (3, 4) strength of gold and platinum in bulk, respectively [18].

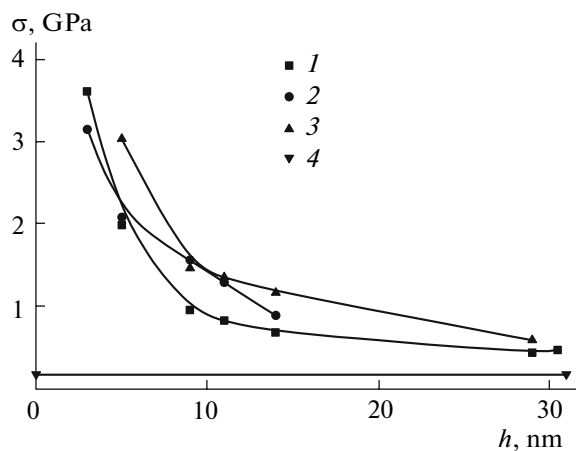


Fig. 5. Strength of gold-based coating vs. its thickness h for (1) PET, (2) PVC, and (3) plasticized PVC; (4) strength of gold in bulk [18]. Strain rate is 0.2 mm/min; 20°C.

180 to 220 MPa; for platinum, from 250 to 300 MPa. These values agree quantitatively with the known values for bulk metals (176–250 MPa for gold and 240–350 MPa for platinum [18]). However, it is noteworthy that, once the thickness of the metallic coating decreases below ~ 15 nm (Fig. 4), the strength of both metals starts to increase dramatically as the thickness of the deposited coating decreases. In this case, the strength achieves 1800 and 3700 MPa for platinum and gold, respectively. As is seen, the strength of a metal in its nanolayers is higher than that of the bulk material by at least one decimal order of magnitude.

This result offers the first quantitative estimation of the strength of metals in ultrathin layers under the conditions of uniaxial tensile drawing. This indicates that the characteristics (in the case under study, the fundamental property of strength) of a substance in nanolayers are actually different from those of the bulk material. However, note that, in this case, we are dealing with the strength not of a pure metal but of a metallic coating deposited onto a polymer support by ionic plasma deposition.

In this connection, the following question arises: what is the possible effect of interaction between a polymer and a coating on the stress–strain characteristics of the coating? Now, let us consider the influence of the nature of a supporting polymer on the strength of the deposited coating. Figure 5 compares the dependences of strength of the gold-based coatings deposited onto various polymeric materials on their thickness. As is well seen, in all cases, the strength of the coating markedly increases as its thickness decreases below 15 nm. When the thickness of the coating is high, the above dependences approach the strength of the bulk metals. It is worth mentioning that, under the selected deformation conditions, the nature of a polymer support exerts no marked effect on the strength of a nanothick gold-based coating

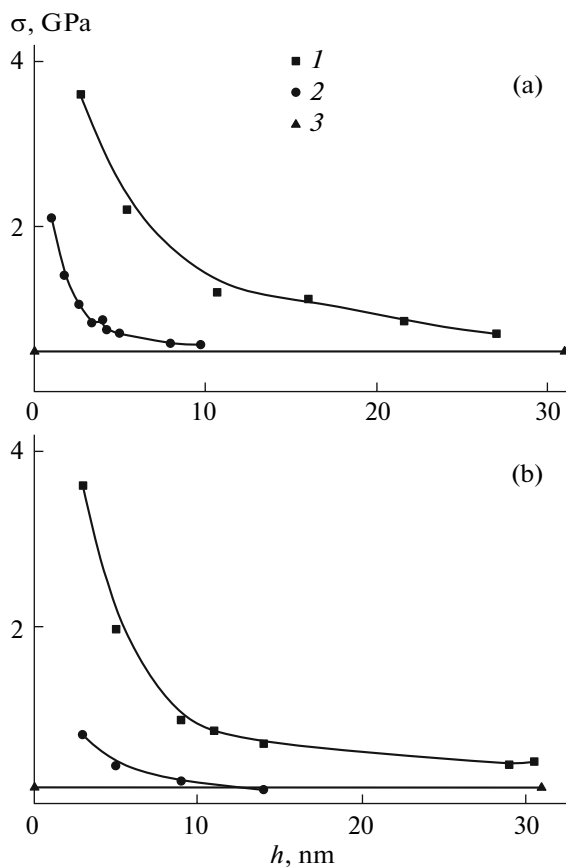


Fig. 6. Strength of (a) gold-based and (b) platinum-based coating vs. thickness upon deformation of PET samples at (1) 20 and (2) 90°C; (3) strength of the metal in bulk [18].

because nearly the entire body of experimental evidence is fairly described by the single dependence of strength on the thickness of the metallic coating.

Figure 5 presents the results obtained for glassy polymers upon their tensile drawing. It is common knowledge that, on passing from the glassy to rubbery state, the stress–strain characteristics of polymers change dramatically [19].

Let us consider how this factor would affect the strength of a metallic coating deposited onto the surface of a supporting polymer. Figure 6 presents the strength of gold and platinum coatings plotted against their thickness at room temperature (below the glass transition temperature) and at 90°C (above glass transition temperature).

First of all, let us mention that, in all cases, the strength of the metallic coating increases with decreasing thickness below a certain level. At the same time, at temperatures below the glass transition temperature of the supporting polymer, the strength of both metallic coatings appears to be much higher than that estimated at temperatures above the glass transition temperature of the polymer support. This difference is observed only when the thickness of the coat-

ings is small, below 10–15 nm. When the thickness is larger, both dependences approach the strength of the bulk metal. The data presented in Fig. 6 allow one to expect that thin deposited coatings (≤ 15 nm) possess certain structural features responsible for this unusual stress–strain response depending on the physical state of the supporting polymer.

In this connection, the following questions arise. What are the reasons behind this growth in strength of metals deposited onto the surface of polymer supports when the thickness of the metallic layer is less than 15 nm? Why does the transition of a polymer from its glassy to rubbery state affect the strength of a metallic coating?

To answer the first question, let us consider how the dimensions of grains of the crystal lattice in solids affect strength. It is common knowledge that the strength of crystalline solids usually increases with as the grains of crystalline structure down to the nanoscale level [20]. In this connection, many scientists have focused their efforts on developing finely grained structure of crystalline bodies and, in particular, of metals. In this respect, the most promising approach, even though not the only one, for this kind of nanostructure in metals is the method of intensive plastic deformation [21]. The principle of this method involves simultaneous action of shear stresses (by high strains) under conditions where a constant volume is maintained. These conditions can be achieved by coupling twisting deformation with hydrostatic pressure, which is required to prevent the development of cracks and pores [22, 23]. This approach makes it possible to prepare allows a uniform finely grained structure with mean dimensions of grains ranging from 100 to 200 nm. This treatment leading to the formation of a finely grained structure has a strong effect on the stress–strain characteristics of the material. This increase in strength and rigidity with decreasing grain dimensions is associated with the emergence of additional grain boundaries, which serve as obstacles preventing the movement of dislocations; once nanoscale dimensions of grains are attained, improvement in strength results from the low density of existing dislocations and prohibited nucleation of new dislocations [24].

The dimensions and shape of grains are very important, but not the only characteristics for developing new properties of nanostructured materials. Another important factor is the structure of grain boundaries. In particular, metals subjected to intensive plastic deformations are characterized by high internal stresses, which are induced by the high density of defects inside crystals and at their boundaries [25].

In essence, the formation of nanometric coatings on the surface of polymer films offers an efficient method for controlling the dimensions of grains characteristic of the structure of metals. Indeed, when the thickness of the coating is several nanometers (Figs. 4–6), the dimensions of grains within this layer cannot exceed this value. As was mentioned, when

metallic grain structure is dispersed down to nanoscale level, all stress–strain characteristics, including strength, are markedly increased. This effect of the dimensions of grains in a crystalline body on its strength can be referred to as the effect of nanostructuring.

Evidently, characteristics of noble metals (Au and Pt) used as materials for the deposited coatings cannot be markedly changed at 20–90°C because their melting temperature is appreciably higher than 1000°C. Therefore, the above dependence (Fig. 6) of the strength of the metallic coating on the temperature of tensile drawing of a supporting polymer is somehow related to the characteristics of this polymer. Below, we present stresses σ_0 for various supporting polymers at 20°C (in the case of PET, at 20 and 90°C):

Support	PET (20/90°C)	PVC	PVC + 15% DOP
σ_0 , MPa	37.7/2.1	24.0	36.0

As is seen, stresses corresponding to the deformation of a polymer support at room temperature appear to be close to each other, independently of polymer nature. As a consequence, the dependences of the strength of the coatings on their thickness are likely to be the same (Fig. 5). At the same time, deformation of PET at 90°C takes place at a stress level lower than that at 20°C by an order of magnitude; it is possible that this behavior is related to the transition of a polymer from its glassy to its rubbery state.

Therefore, one can expect that the above dependence of the strength of the coating on the temperature of deformation of the supporting polymer is a result of certain structural features of the polymer–metal system. Analysis of the literature data shows that interaction between polymers and atoms at the atomic and nanoscale levels actually takes place. In particular, penetration of metallic Ga to polymers (PE, PS, PI, PET (semicrystalline) and PTFE) has been studied in [26]. As was shown, Ga is able to penetrate into polymers only from its liquid phase ($T_m = 29.8^\circ\text{C}$) and its overall content in polymers increases with increasing temperature and duration of its contact with the polymer. The content of Ga in the surface layer is inversely proportional to the polymer density. It is important to mention that the concentration of Ga decreases on moving from the polymer surface into its volume by a depth of ~ 200 nm.

Another approach to the incorporation of metals into the polymer surface layer has been used in [27]. The surface of a PC was decorated with a thin gold layer; then, the coated film was allowed to remain in acetone vapors. Acetone is known to induce the crystallization of PC and seemingly assists the migration of metal atoms into the bulk polymer; as a result, the sectioned surfaces of the crystallized samples reveal the population of gold nanoparticles with dimensions of

8–10 nm. In [28], interaction between various polymers and gold sputtered onto the polymer surface by ionic plasma deposition was studied by X-ray photoelectron spectroscopy. This approach visualizes the development of an interfacial metal–polymer boundary starting from the moment when the first metal atoms appear on the polymer surface until a continuous metallic coating is formed. As was found, in the course of ionic plasma deposition, metal atoms can penetrate the bulk polymer to a depth of ~10 nm.

Thermal sputtering also allows penetration of metals into polymers even though, in this case, the energy of sputtered metallic atoms is much lower. For example, penetration of copper atoms into biaxially oriented PET films was studied by the Rutherford backscattering spectroscopy [29]. In the polymer surface layer, it was found that a diffuse metallic layer forms. The depth of metal penetration is 50–60 nm.

In [30], direct TEM observations of ultrathin sectioned samples proved that, in the course of thermal sputtering, metal atoms are able to penetrate a glassy polymer to a depth of 200 nm and, in the vicinity of the polymer–metal interface, they form the system of metallic nanoclusters with dimensions of 5–10 nm.

Important results have been reported in [31], where direct microscopic data on the fragmentation of thin metallic layers on the polymer surface in the course of deformation have been analyzed. In this work, the authors proposed the existence of a certain interfacial layer at the polymer–metal boundary, which is an ultrafine mixture of incompatible components (a metal and a polymer). In this case, it is noteworthy that the mechanical characteristics of this interfacial layer are higher than those of the pure supporting polymer.

The following question arises: how do thermodynamically incompatible components form the above ultrafine interfacial layer? The reasons for the development of this interfacial layer make it possible to understand the results of scientific studies performed during the recent decade. As was unequivocally shown, surface layers of glassy polymers have a strongly depressed glass transition temperature or, in other words, an increased free-volume content [32–34]. This loosened polymer surface layer with its increased free-volume content is permeable to the high-energy flow of metal atoms generated upon thermal or ionic plasma deposition. For this reason, metal atoms effectively penetrate the polymer surface layer to a depth of 5–10 nm [35, 36], where they merge into nanoclusters with dimensions of several nanometers. As a result, an ultrafine nanodispersed polymer–metal mixture is formed and its phase dimensions are on the order of several nanometers. Penetration of a metal into the polymer surface layer dramatically changes its mechanical characteristics. Prior to metal precipitation, the polymer surface layer is characterized by a depressed glass transition temperature (as compared with the glass transition temperature of the bulk poly-

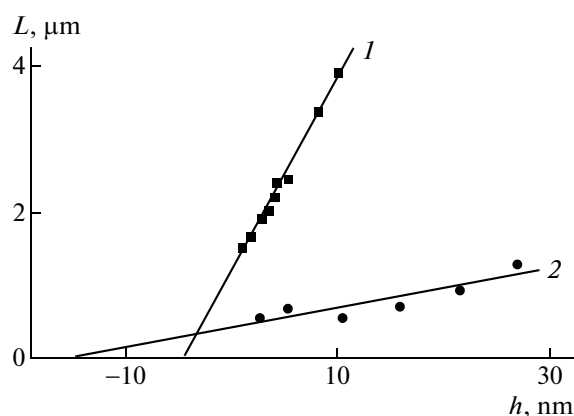


Fig. 7. Mean dimensions of the fractured fragments of the platinum-based coating deposited onto PET films vs. thickness. The polymer support is stretched by 100% at 90°C with a strain rate of (1) 10 and (2) 0.2 mm/min at room temperature via necking.

mer) or it even exists in its rubbery state [37, 38]. After metal deposition onto the polymer surface or, in other words, after the incorporation of metal atoms into the rubbery polymer surface layer, glass transition temperature of this layer increases and, hence, the mechanical characteristics appear to have been improved as compared with those of the bulk polymer. This reinforcement of elastomers with the dispersions of inorganic fillers is a well-known phenomenon widely used in practice [39].

Figure 7 presents certain additional proof supporting the existence of the interfacial layer at the polymer–(metallic coating) boundary. Figure 7 shows mean dimensions L of the fractured fragments of the platinum-based coating plotted against its thickness for two different modes of deformation of polymer support. As is well seen, L is directly proportional to the thickness of the coating h , in full agreement with Eq. (1). Nevertheless, even though L and h are directly related to each other, the above dependence does not pass through zero, whereas this behavior is predicted by Eq. (1). Extrapolation of the dependence of L on h to the abscissa axis gives 5–10 nm. Hence, one can expect that the coating has a certain extra thickness, which can be estimated by extrapolating the dependences of the surface relief parameters on thickness. At the same time, the calibration curve shown Fig. 2 passes through zero. This implies that the polymer actually does have a certain loosened layer with a thickness of 5–10 nm, whereas an inorganic glass is free of this structural attribute.

Let us consider certain structural features of thin nanoscale layers deposited onto polymer films by using the method of transmission electron microscopy. Figure 8 presents the typical results of this microscopic examination. This suggests that metals deposited onto a polymer support by ionic plasma deposition exhibit a finely grained structure. In the above nanolayers, the

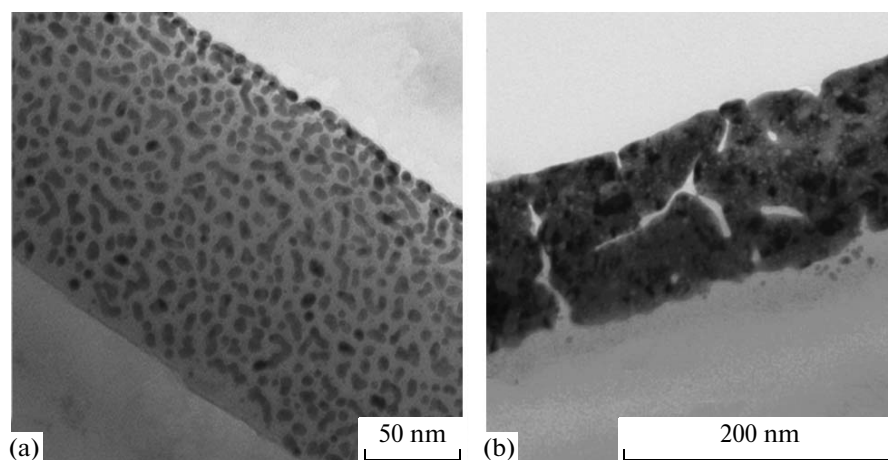


Fig. 8. TEM images of ultrathin sections of gold-coated PET samples; the thickness of the gold-based coating is (a) 3 and (b) 30 nm.

dimensions of metallic grains range from several nanometers to tens of nanometers, depending on the thickness of the coating. When the thickness is small (in the interval in which the strength of a metal increases), the coating can be visualized as a certain nanocomposite in which small-sized metallic crystallites (nanoparticles) alternate with polymer partitions (Fig. 8a).

If this structural pattern illustrating a polymer with a deposited metallic coating is correct, one can endeavor to gain insight into the effect of how the mechanical characteristics of a polymer affect the strength of a metallic coating deposited onto a polymer surface. Evidently, this effect is observed only for thin coatings where the effect of nanostructuring takes place. Figure 9 presents this curve describing the strength of the platinum-based coating with a thick-

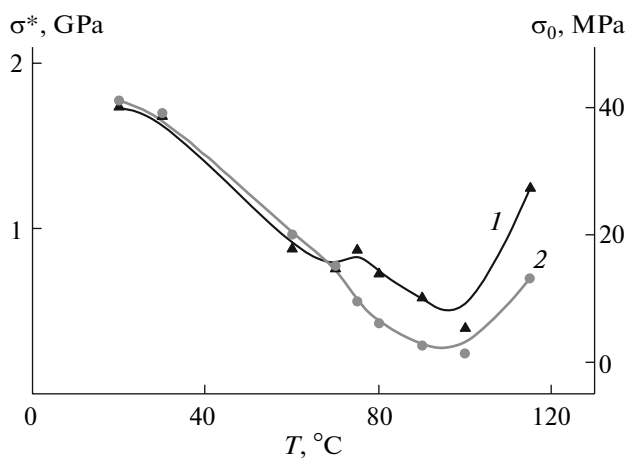


Fig. 9. Temperature dependences of (1) strength σ^* of the coating for amorphous PET with platinum coating with a thickness of 3.8 nm and (2) stress σ_0 in PET support upon its tensile drawing with a strain rate of 0.1 mm/min.

ness of 3.8 nm plotted against the temperature of tensile drawing, and this curve is compared with the temperature dependence of stress on the PET support. The correlation between the above dependences is obvious. Starting with room temperature, the strength of the coating (curve 1) gradually decreases, similar to the stress on the PET support (curve 2). However, at temperatures above 100°C, strength of the coating increases dramatically. Within this temperature interval, stress on the support also increases and this tendency is likely to be related to the crystallization of PET upon its heating above 100°C.

In the deformed PET, mechanical stress can be affected not only by temperature but also by the environment, which controls the mechanism of polymer deformation from necking to classical crazing [40]. In [41], surface structuring was studied for the deformation of PET with a deposited thin (3.8 nm) platinum coating upon its tensile drawing in the presence of an adsorptionally active liquid environment (AAL) (*n*-decanol-1). Figure 10 presents the results of these studies. Similar to Fig. 9, Fig. 10 compares the temperature dependences of the strength of the coating (curve 1) estimated by means of Eq. (1) and stress providing tensile drawing (curve 2). As is seen, for PET, the whole temperature dependence of stress is shifted to lower values (cf. Figs. 9 and 10). However, this is not the only effect of a liquid environment. As is well known, upon heating up to the glass transition temperature, an AAL effectively penetrates the PET, and this process is accompanied by intensive crystallization of the polymer [42]. For this reason, starting at about 85°C, the stress in the deformed PET increases markedly (curve 2). As also follows from Fig. 10 (curve 1), the AAL strongly affects the strength of the coating. First, the strength appears to be significantly lower than that of PET upon its stretching in air (cf. Figs. 9 and 10). Second, the temperature dependence of the strength of the coating correlates well with the

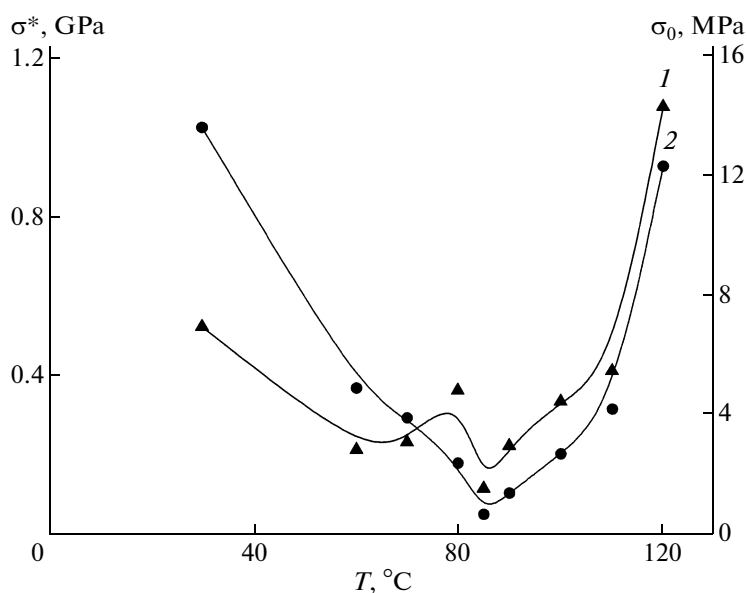


Fig. 10. (1) Strength σ^* of the platinum-based coating with a thickness of 3.8 nm and (2) stress σ_0 in PET support upon its tensile drawing in *n*-decanol-1 vs. temperature; strain rate is 0.1 mm/min.

stress on the PET support. This unequivocally suggests that the above factors (temperature and AALE) control the strength of the coating by affecting the characteristics of supporting polymer. As follows from Figs. 4 and 5, this effect is most pronounced when the thickness of the deposited coating is low (≤ 15 nm).

This allows us to conclude that the interfacial layer formed at the early stages of metal deposition, which can be represented as a certain nanocomposite, is characterized by a higher strength as compared with that of a pure metal deposited onto this layer. This conclusion is indirectly supported by the following: first, the dimensions of metallic grains in the interfacial layer are smaller than those in a pure metal and, second, the intergrain distance in this layer is filled with a polymer phase (polymer matrix). Evidently, both factors favor an increase in the strength of the interfacial layer as compared with the strength of a pure metal deposited onto the above interfacial layer. At the same time, both the temperature and AALE exert their action on polymer partitions within this interfacial nanocomposite and thus control the overall strength of the coating when its thickness is small (≤ 15 nm).

This experimental evidence allows us to propose the following scenario leading to the development of the polymer–(metallic coating) system (Fig. 11). The initial polymer has a loosened surface layer with a high content of free volume (Fig. 11a). When the metal is sputtered onto the surface of a polymer support, the early stages are accompanied by the penetration of metallic atoms into the loosened surface layer. As this layer is loaded with metal, a robust surface nanocomposite layer on the polymer surface is formed and

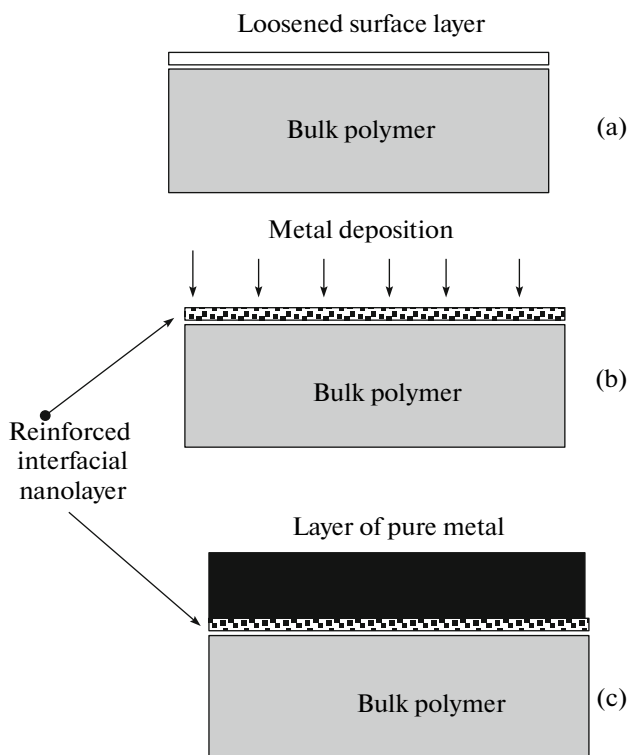


Fig. 11. Scheme of structural rearrangements taking place during deposition of a metallic coating onto a polymer surface: (a) initial polymer film, (b) development of an interfacial layer at the early stages of metal deposition, (c) schematic representation of a polymer with a deposited metallic coating.

thickness of this layer is ~10 nm (Fig. 11b). The high strength of this layer results from the finely grained structure of the metal and from the mutual connectedness of metallic grains throughout the polymer matrix. Further metal deposition onto the polymer surface is accompanied by the development of a layer composed of a pure metal, and structure of this layer resting on the strengthened interfacial layer contains bigger metallic grains (Fig. 11c). With the increasing thickness of this layer, the contribution from the interfacial high-strength layer to the total strength of the coating gradually decreases. When the overall thickness of the coating is high, the contribution from the interfacial sublayer is small and the total strength of the coating is primarily controlled by the strength of the relatively thick layer of a pure metal. Evidently, the strength of the pure metal does not depend on the characteristics of the supporting polymer. Hence, when the thickness of the coating is high, its strength gradually decreases independently of the nature and state of the supporting polymer and approaches the strength of the bulk metal (Figs. 3, 4).

REFERENCES

1. Y. Leterrier, L. Boogh, J. Anderson, and J.-A. E. Manson, *J. Polym. Sci., Part B: Polym. Phys.* **35**, 1449 (1997).
2. Y. Leterrier, L. Boogh, J. Anderson, and J. E. Manson, *J. Polym. Sci., Part B: Polym. Phys.* **35**, 1463 (1997).
3. J. T. Felts, *J. Plast. Film Sheeting* **9**, 201 (1993).
4. G. B. Sergeev, *Nanochemistry* (Mosk. Gos. Univ., Moscow, 2003) [in Russian].
5. I. P. Suzdalev, *Nanotechnology. Physical Chemistry of Nanoclusters, Nanostructures and Nanomaterials* (KomKniga, Moscow, 2006) [in Russian].
6. S. S. Ivanchev and A. N. Ozerin, *Polymer Science, Ser. B* **48**, 213 (2006) [*Vysokomol. Soedin., Ser. B* **48**, 1531 (2006)].
7. Y. Xiang, X. Chen, T. Y. Tsui, et al., *J. Mater. Res.* **21**, 386 (2006).
8. X. Chen and J. J. Vlassak, *J. Mater. Res.* **16**, 2974 (2001).
9. S. U. Jen and T. C. Wu, *Thin Solid Films* **492**, 166 (2005).
10. A. L. Volynskii, S. L. Bazhenov, and N. F. Bakeev, *Russ. Khim. Zh.* **42** (3), 57 (1998).
11. A. L. Volynskii, S. L. Bazhenov, O. V. Lebedeva, and N. F. Bakeev, *J. Mater. Sci.* **35**, 547 (2000).
12. A. L. Volynskii, S. L. Bazhenov, O. V. Lebedeva, et al., *J. Appl. Polym. Sci.* **72**, 1267 (1999).
13. S. L. Bazhenov, A. L. Volynskii, V. M. Alexandrov, and N. F. Bakeev, *J. Polym. Sci., Part B: Polym. Phys.* **40**, 10 (2002).
14. A. L. Volynskii, S. V. Moiseeva, L. M. Yarysheva, and N. F. Bakeev, *Dokl. Akad. Nauk* **409**, 64 (2006).
15. A. S. Filonov and I. V. Yaminskii, *FemtoScan Program Package for Three-Dimensional Image Processing* (Tsentr Perspektivnykh Tekhnologii, Moscow, 2006) [in Russian], <http://www.nanoscopy/net>.
16. A. L. Volynskii, *Nauka Ross.*, No. 3, 4 (2002).
17. A. L. Volynskii, E. E. Voronina, O. V. Lebedeva, et al., *Dokl. Akad. Nauk* **360**, 205 (1998).
18. *Handbook of Chemistry and Physics*, Ed. by Ch. D. Hodgman (New York, 1955), p. 1982.
19. V. E. Gul' and V. N. Kuleznev, *The Structure and Mechanical Properties of Polymers* (Khimiya, Moscow, 1972) [in Russian].
20. M. Gutkin and I. A. Ovid'ko, *Defects and Mechanisms of Plasticity in Nanostructured and Noncrystalline Materials* (Yanus, Moscow, 2000) [in Russian].
21. N. P. Lyakishev and M. I. Alymov, *Russ. Nanotekhnol.* **1**, 71 (2006).
22. O. A. Kaibyshev and F. Z. Utyashev, *Superplasticity, Structural Grinding and Treatment of Difficultly Deformable Alloys* (Nauka, Moscow, 2002) [in Russian].
23. F. P. Zhilyaev, S. Lee, G. V. Nurislamova, et al., *Scr. Mater.* **44**, 2757 (2001).
24. R. W. Siegel and G. E. Fougere, *Nanostruct. Mater.* **6**, 205 (1995).
25. I. V. Aleksandrov, A. R. Kil'mametov, and R. Z. Valiev, *Metally* **1**, 63 (2004).
26. V. Svorchik, K. Efimenko, V. Rubka, and V. Hnatowicz, *Appl. Phys. A* **68**, 357 (1999).
27. K. K. K. Koziol, K. Dolgner, N. Tsuboi, et al., *Macromolecules* **37**, 2182 (2004).
28. A. I. Pertsin and Yu. M. Pashunin, *Polymer Science, Ser. B* **38**, 231 (1996) [*Vysokomol. Soedin., Ser. B* **38**, 919 (1996)].
29. P. A. Gollier and P. Bertrand, *Vide Couches Minces* **50**, 99 (1994).
30. V. Zaporozhchenko, T. Strunskus, K. Behnke, et al., *J. Adhes. Sci. Technol.* **14**, 467 (2000).
31. A. L. Volynskii, S. V. Moiseeva, A. I. Dement'ev, et al., *Polymer Science, Ser. A* **48** (2006) [*Vysokomol. Soedin., Ser. A* **48**, 1125 (2006)].
32. J. A. Forrest and K. Dalnoki-Veress, *Adv. Colloid Interface Sci.* **94**, 167 (2001).
33. J. A. Forrest, *Eur. Phys. J., E* **8**, 261 (2002).
34. M. Bhattacharya, M. K. Sanyal, Th. Geue, and U. Pietsch, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **71**, 041801 (2005).
35. X. Zheng, B. B. Sauer, J. G. Van Alsten, et al., *Phys. Rev. Lett.* **74**, 407 (1995).
36. J. Hyun, D. E. Aspens, and J. J. Cuomo, *Macromolecules* **34**, 2396 (2001).
37. T. Kajiyama, K. Tanaka, N. Satomi, and A. Takahara, *Sci. Technol. Adv. Mater.* **1**, 31 (2000).
38. Y. M. Boiko and R. E. Prudhomme, *Macromolecules* **31**, 6620 (1998).
39. Yu. S. Lipatov, in *Encyclopedia of Polymers* (Sovetskaya Entsiklopediya, Moscow, 1974) [in Russian].
40. A. L. Volynskii and N. F. Bakeev, *Solvent Crazing of Polymers* (Elsevier, Amsterdam, 1996), p. 410.
41. O. V. Lebedeva, Candidate's Dissertation in Chemistry (Moscow, 2000).
42. A. L. Volynskii and N. F. Bakeev, *Highly Dispersed Oriented State of Polymers* (Khimiya, Moscow, 1984) [in Russian].