

Structure and Properties of the Polymer–Metal Coating Interface Layer

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Recent studies have shown that application of metal coatings to polymers gives rise to a certain transition layer consisting of a fine polymer mixture with metal nanoclusters. However, the properties, in particular, deformation-strength properties of this nanolayer remain unknown. Recently [1], a new approach to characterizing the deformation-strength properties of solids in nanolayers has been proposed. In this work, we evaluate these properties for nanocoatings applied to the surface of polymer films. Deformation of coated polymer films is accompanied by the formation of a special sort of relief, the parameters of which contain information on the mechanical properties of the coating material. The previously revealed [2–4] relationship between the directly determinable parameters of the relief and the properties of the coating material underlay the method [1] for evaluating the mechanical properties of nanosolids. Whether the deformation of the yielding support is uniform or not, the average size L of a cracked-coating fragment along the stretching axis is [2, 4]

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

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

Thus, the properties of deformation of a polymer support coated with a thin solid layer relate the strength of solids, their important characteristic, to the average size L of cracked-coating fragments produced in deformation of polymer films coated with a thin solid layer. This fragment size is easy to determine in direct microscopic experiments. Essentially, the found relationship underlies a simple direct method for evaluating the deformation-strength properties of solids in layers of any thickness, including nanolayers.

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Previously [5, 6], for evaluating the plastic strain of metal layers applied to the surface of polymer films, we also developed a method for making this evaluation using direct microscopic data. Obviously, $L_{\text{coat}} = \sum L_n = 1 + \epsilon_{\text{coat}}$, where L_{coat} is the sum of the lengths of cracked-coating fragments on the support, ϵ_{coat} is the irreversible strain, and n is the number of cracked-coating fragments. Hence,

$$\epsilon_{\text{coat}} = \left(\frac{L_{\text{coat}}}{L_{\text{total}}} \cdot \lambda_{\text{polym}} - 1 \right), \quad \% \quad (2)$$

where L_{total} is the length of the portion of the support film on which the sum $\sum L_n$ of the lengths of cracked-coating fragments is measured, and λ_{polym} is the support-film elongation determined by the stretching machine.

Equation (2) implies that the plastic strain of the coating is easy to find by directly measuring L_{coat} , L_{total} , and λ_{polym} on photomicrographs.

In this work, the deformation-strength properties of metal nanocoatings applied to polymer films were evaluated for the first time by the new direct universal method. It was found that, with a decrease in the coating thickness, beginning with approximately 15 nm, the strength of the coating, regardless of its nature, begins to significantly increase and becomes at least an order of magnitude higher than the strength of the bulk metal. To explain this phenomenon, we formulated a three-layer model of the polymer–coating system, in which a strengthened nanolayer at the polymer–coating interface is assumed to exist. The theoretical and experimental data were found to be in good agreement, which confirmed the adequacy of the model proposed.

In the experiment, 100- μm -thick commercial amorphous unoriented poly(ethylene terephthalate) films were used. Dumbbell test specimens with a size of the working part of 6×20 mm were cut out from these films. Thin platinum or gold layers of various thicknesses were applied to the specimen surface by ion plasma sputtering with an Eiko IB-3 ion coater. Dynamic measurements were made on an Instron-1122

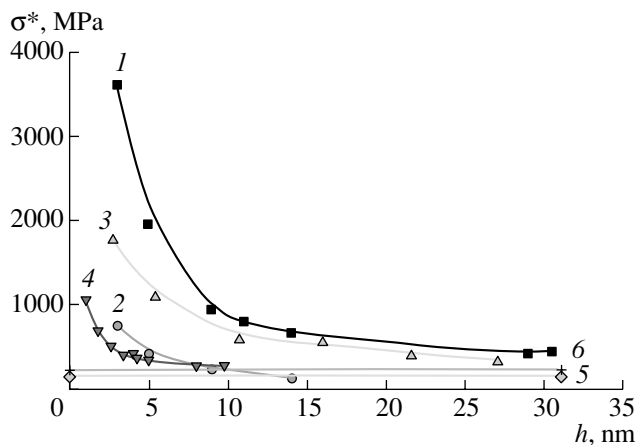


Fig. 1. (1, 2) Gold and (3, 4) platinum coating strengths σ^* at (1, 3) 20 and (2, 4) 90°C versus coating thickness. Lines 5 and 6 represent the bulk gold and platinum strengths, respectively.

tension meter and tension machine. Specific features of surface structuring in deformation of polymer films coated with thin metal layers were studied with a Hitachi S-520 scanning electron microscope. The numerical values of the average sizes of cracked-coating fragments were found from electron photomicrographs using the FemtoScan Online software [7].

Figure 1 presents typical results of such a study. It is well seen that the strengths of both metals are virtually independent of their layer thickness within the range of 30 to ≈ 15 nm. The gold and platinum strengths within this range are 180–220 and 250–300 MPa, respectively. These values agree quantitatively with the known strength values for bulk metals (176–250 and 240–350 MPa for gold and platinum, respectively [10]). At the same time, Fig. 1 demonstrates that, beginning with a thickness of approximately 15 nm, the strengths of both metals abruptly increase with a decrease in the coating thickness. The platinum and gold strengths reach 1800 and 3700 MPa, respectively. The metal strength in 3 nanolayers is seen to be at least an order of magnitude higher than the strength of the bulk material. Note that the coating strengths are strongly affected by the support-film deformation temperature. As Fig. 1 shows, this effect is observed only at small coating thicknesses (within ~ 15 nm). At larger thicknesses, the coating strength becomes independent of the deformation temperature and tends to the bulk metal strength.

The following questions arise.

Why does the coating strengths abruptly increase with a decrease in the coating thickness at small thicknesses (less than 10–15 nm)?

Why does this increase depend on the polymer-support deformation temperature?

Why does the polymer-support strength at coating thicknesses more than 10–15 nm become independent

of the deformation temperature and tend to the bulk metal strength?

Nanostructuring of crystalline bodies (decrease in the crystal grain size to the nanolevel) is generally accompanied by a multifold increase in their strength [8]. The main methods of such nanostructuring are powder metallurgy (nanopowder compaction), crystallization from an amorphous state, intense plastic deformation, and various techniques of application of nanostructured coatings. It is probably the last example of nanostructuring that is observed in Fig. 1 since the decrease in the coating thickness means a decrease in the metal crystal grains to the nanolevel. If this is the case, then the increase in the coating strength should be accompanied by a decrease in its plasticity [8]. This phenomenon is caused by the fact that nanostructuring of crystalline bodies, in particular, metals, is induced by obstacles to the motion of dislocations at crystal grain boundaries. At the same time, it is the motion of dislocations in crystalline bodies that is responsible to their plastic deformation. Consequently, if, in the metal coatings studied, a dislocation mechanism of deformation occurs, then, with an increase in the strength, their plasticity must decrease.

To test this assumption, we investigated the plasticity (irreversible strain) in deformation of the polymer support (Eq. (2)). Figure 2 presents typical results of this study. It is seen that, regardless of the nature of the metal coating and the polymer-support deformation temperature, the plastic strain of the coating abruptly increases at small coating thicknesses (less than 10–15 nm). The result obtained means that, in the coating at small thicknesses, a dislocation mechanism of deformation does not occur.

All the observed anomalies in the deformation-strength properties of the coatings are at small coating thicknesses (less than 10–15 nm). At the same time, the data in Fig. 1 show that the coating strength changes significantly with a change in the polymer-support deformation temperature by 70°C (from room temperature to 90°C). The melting points of both metals (gold and platinum) exceed 1000°C, and it is difficult to imagine any causes that could sharply change their strengths within such an insignificant temperature range. Hence, the coating properties should somehow be affected by the strength properties of the polymer support.

It is known [9–11] that, in application of metal coatings by thermal or ion plasma sputtering to a vitreous polymer, metal atoms penetrate the surface layer of the polymer. This penetration gives rise to a certain transition layer consisting of an ultrafine (nanosized) dispersion of metal clusters incorporated in the polymer. This layer can emerge because, on the surface of vitreous polymers, there is a thin layer of loose material the glass-transition temperature of which is lower than that of the bulk polymer by tens and even hundreds of degrees. The thickness of this layer is about 5–15 nm

[12], which is likely to determine the depth of metal penetration into the polymer during thermal or ion plasma sputtering. It can be assumed that the increase in the strength and plasticity of the coatings at small thicknesses is related to the properties of this transition layer, rather than caused by a change in the properties of the pure metal in thin nanolayers.

To test this assumption, let us consider a thin coating consisting of two layers. Let the strength of layer 1 (sublayer) of thickness h_1 be σ_1 and the strength of layer 2 (pure metal layer on the sublayer) of thickness h_2 be σ_2 ; then, while the coating is cracking, it carries the load

$$F = \sigma_1 h_1 w + \sigma_2 h_2 w,$$

where w is the coating (specimen) width. The effective strength of the coating in this case is found by dividing the total applied force F to the cross-sectional area $w(h_1 + h_2)$ of the coating:

$$\sigma_c = \frac{\sigma_1 h_1 + \sigma_2 h_2}{h_1 + h_2},$$

where σ_c is the total strength of the coating, which is found from Eq. (1) and which depends on the total thickness of the coating as shown in Fig. 1. This dependence can be described by the equation

$$\sigma_c(h_1 + h_2) = \sigma_1 h_1 + \sigma_2 h_2. \quad (3)$$

If the assumption on the two-layer structure of the coating is valid, this equation should describe a linear dependence of the experimental strength σ_c (Fig. 1) on the total thickness of the coating. The results obtained are shown in Fig. 3.

It turned out that the experimental data presented in Fig. 1 are perfectly (correlation coefficient 0.9999) approximated by a straight line described by Eq. (3). The slopes of these straight lines indicate the strengths of the bulk metals. These values for gold and platinum were found to be 180 and 240 MPa, respectively (the strengths of bulk gold and platinum are 176–250 and 240–350 MPa, respectively [13]). It also proved that the slopes of the lines for gold and platinum that are found from the data in Fig. 3 coincide at polymer-support deformation temperatures of 20 and 90°C. This means that the strengths of these metals in the bulk are also independent of either temperature within the given temperature range, or the presence of the polymer support.

Figure 3 also implies that the sublayer strength multiplied by the sublayer thickness as determined from the y-intercept depends critically on the deformation temperature. Naturally, the deformation-strength properties of the studied support polymer (poly(ethylene terephthalate)) with a glass-transition temperature of 75°C change significantly in the temperature range of 20 to 90°C, and this affects the deformation-strength properties of the nanocomposite sublayer, where the polymer is, in essence, a binder.

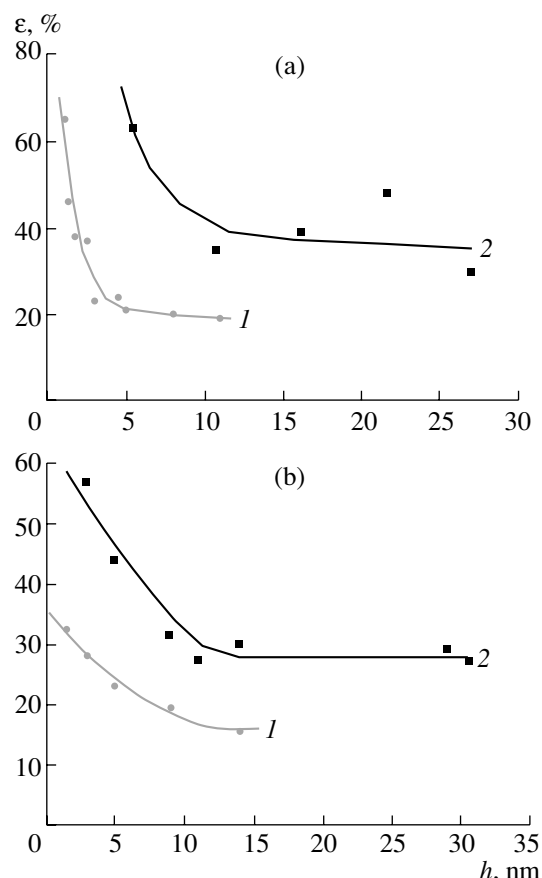


Fig. 2. Plastic strains ε of the (a) platinum and (b) gold coatings at (1) 90 and (2) 20°C versus coating thickness.

Thus, the totality of the experimental data considered suggests the following pattern of events accompanying the emergence of the polymer–metal coating system. On the initial polymer, there is a loose surface layer of a thickness of about 10 nm with a large void volume fraction. Early in metal sputtering to the surface of the polymer support, metal atoms penetrate the loose surface layer. The saturation of this layer with metal is accompanied by the emergence of a strong surface composite nanolayer of a thickness of about 10 nm on the polymer surface. This layer has high strength owing to the fine-grain structure of the metal and the binding of metal grains to one another with polymer interlayers. Further metal application to the polymer surface gives rise to a pure metal layer with larger-grain structure on the strengthened interface layer. The increase in the thickness of this layer gradually decreases the contribution of the strengthened interface layer to the total strength of the coating. At relatively large coating thicknesses, the contribution of the interface sublayer is small and the coating strength is mainly determined by the strength of the relatively thick pure metal layer lying above this sublayer. Naturally, the strength of a pure metal is independent of and cannot be dependent on the properties of the polymer support. This is the

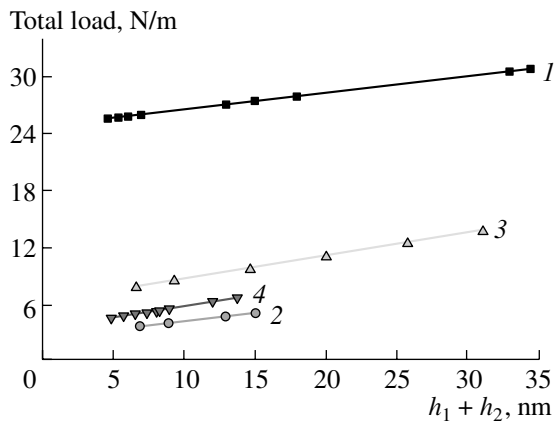


Fig. 3. Total loads on the (1, 2) gold and (3, 4) platinum coatings at (1, 3) 20 and (3, 4) 90°C versus total coating thickness.

reason why the coating strength at relatively large coating thicknesses gradually decreases, regardless of the nature and state of the polymer support, and tends to the strength of the bulk metal.

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