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Study of polystyrene surface local mechanical properties by the atomic force microscopy

ANNA V. ZAITSEVA[1*], VICTOR M. RUDOY[2],
OLGA V. DEMENT'EVA[2], MARIA E. KARTSEVA[2]

[1]M. V. Lomonosov Moscow State University, Physics Department

[2]Institute of Physical Chemistry RAS, Moscow

Composites with polymer surface layer serving as a matrix for metal nanoparticles stabilization are very promising materials for modern nano- and optoelectronics, nonlinear optics, catalysis, chemical sensors and biosensors. Successful development of such nanocomposites is impossible without intimate knowledge of polymer surface layer properties (structural, mechanical, chemical, electrical, etc.) at a nanolevel. In this study, local mechanical properties (elastic modulus, wearing qualities) of polystyrene surface layer were investigated by means of atomic force microscopy (AFM). Elastic modulus was determined from the analysis of force–distance curves within the framework of Johnson–Kendall–Roberts model. A significant decrease of elastic modulus near the polystyrene surface relative to its bulk value was observed. Strong dependence of the surface layer mechanical properties on the polymer molecular weight was found. The influence of different types of treatment (annealing, UV-irradiation) on the polystyrene surface layer mechanical properties was investigated. Strong correlations between PS surface layer mechanical properties and its glass transition temperature variations (studied in our previous works) are discussed.

Key words: *nanostructures; polymer surface; glass transition; nanomechanics; atomic-force microscopy*

1. Introduction

Composites consisting of polymer matrix reinforced with metal nanoparticles have recently begun to attract increasing attention of researchers. It is desirable in many cases that specific properties of a material (electrical, optical, catalytic etc.) be exhibited by its surface or thin near-surface layer while the polymer bulk should retain its initial properties.

One of the most promising routes of formation of such systems is, in our opinion, the deposition of nanoparticles onto polymer from the metal hydro- or organosols followed by the heat treatment of the system. Such an approach allows us to deal with

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[*] Corresponding author, e-mail: vz@hofme.phys.msu.su.

almost monodisperse particles, varying (with high accuracy and over a wide range) their concentration on a polymer surface as well as size and surface chemistry of nanoparticles. Alongside with preliminary modification of a polymer surface layer, it provides a basic capability to create 'two-dimensional' ordered arrays of nanoparticles that are completely or partially embedded into the polymer. In the case of glassy polymer the possibility of designing such 'two-dimensional' nanocomposites arises from the significant difference in polymer surface ($T_{g,s}$) and bulk ($T_{g,b}$) glass temperature [1–3] in a system thermally treated at the temperature T between $T_{g,s}$ and $T_{g,b}$ (this opportunity was shown by us earlier in [4]).

The information on the properties of polymer surface layer (in particular, mechanical ones) at a nanolevel is necessary for realization of the above-mentioned approach to nanocomposites design. Local probing of surface structure and mechanical properties (elastic modulus, frictional and adhesive forces, shear stress, etc.) with a submicron resolution became possible after the introduction of atomic force microscopy (AFM) [5].

2. Experimental

The experiments were performed with polystyrene (PS) films of different molecular weights (M = 270 000, 50 000 and 8700) cast from toluene solutions onto silicon plates (the films thickness was ~1 μm). The samples were stored at ambient conditions during 1–2 days for solvent evaporation. Then some of the high-molecular-weight samples (M = 270 000) were irradiated over 30–120 min in air with a full light of a PRK-4 mercury lamp or annealed at 120 °C during 2.5 hours, while others were left untreated.

The polymer surfaces were investigated using a 'Nanoscope IIIa' (Digital Instruments, USA) atomic-force microscope (AFM) operated in air. To evaluate nanomechanical properties of the polymer surface layers we analyzed 10–20 force-distance curves measured at 5–10 randomly selected locations, using an approach-retract frequency in the range of 0.1–1.0 Hz. We limited ourselves to the analysis of the approaching part of the force–distance curves during intimate repulsive contact. Silicon cantilevers (Digital Instruments) with spring constants varied in the range of 20–50 N/m and tip radii in the range of 20–50 nm were used.

The PS surface native microroughness was observed in the non-disturbing tapping mode AFM while the surface wear experiments were performed in contact mode according to the following scheme: at first, square region (1×1 μm) was scanned with the 50 nN loading force, then the loading force was minimized and a larger image of the surface (around before-scanned region) was taken. After that the residual deformations could be clearly observed.

The analysis of all AFM images was performed with the FemtoScan001 software [6].

3. Results and discussion

To calculate the elastic (Young) modulus from the force-distance curves obtained for the PS surface layers we used the Johnson–Kendall–Roberts (JKR) approach [7]. In contrast to commonly used Hertz approach [8], JKR model takes into account adhesion forces between tip and polymer surfaces and hence gives more reliable results for small indentation depths. In the framework of JKR model, one can obtain the following relation between the Young modulus *E* and indentation depth *h*:

$$E = \frac{9}{4}(1 - \nu^2)Rk\Delta\left[\frac{P_1}{3Rh}\right]^{3/2}$$

where

$$P_1 = 2(P_2 - 1)\left[\frac{1}{9}(P_2 + 1)\right]^{1/3}, \qquad P_2 = \left(\frac{z_{\text{def}}}{\Delta} + 1\right)^{1/2}$$

ν – Poisson ratio ($\nu = 0.33$ for PS), R – tip radius, k – cantilever spring constant, z_{def} – measured vertical deflection of the cantilever and Δ – the cantilever deflection at the point where the tip loses contact with the surface.

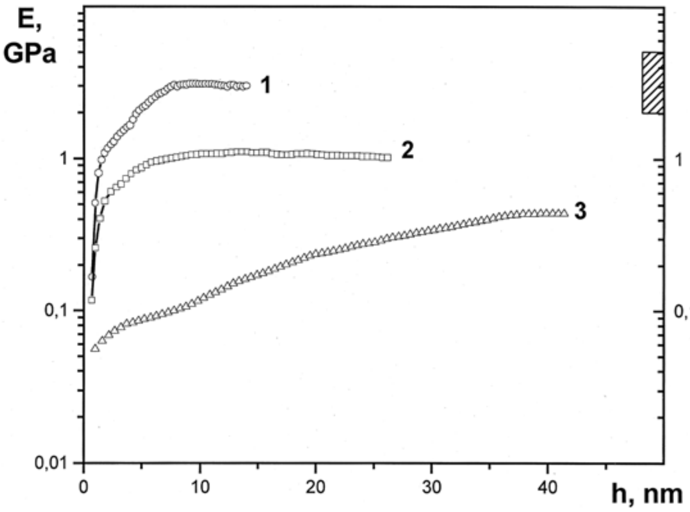

Fig. 1. The Young modulus versus indentation depth for PS with molecular weights $M = 270\ 000$ (1), 50 000 (2) and 8700 (3)

The results of Young modulus determination for PS films with different molecular weights are shown in Fig. 1 (the experimental errors were about 10–15%). The most important feature of the plots in Fig. 1 is a significant decrease of the elastic modulus (for an order and more) near the polymer surface (below 7–30 nm in depth). At higher indentation depths, the values of Young moduli become constant, which corresponds with a high accuracy to the bulk polymer modulus (the bar on the right represents the bulk Young modulus range for PS M = 270 000). The effect of elastic modulus decrease at small indentation depths correlates with our previous measurements of the PS surface layer glass transition temperature ($T_{g,s}$) which turned out to be sufficiently lower on the depths of 15–20 nm than its bulk value [9, 10]. Both effects must arise from the fact that polymer chains possess an additional degree of freedom near the surface. Our results suggest that PS thin surface layer may be in some intermediate state between glassy and rubber-like (or even liquid-like). In our previous works, we found out that $T_{g,s}$ decreases with molecular weight decrease (especially sharply for $M < 20\ 000$–30 000) and, as it is seen from Fig. 1, the same happens with Young modulus.

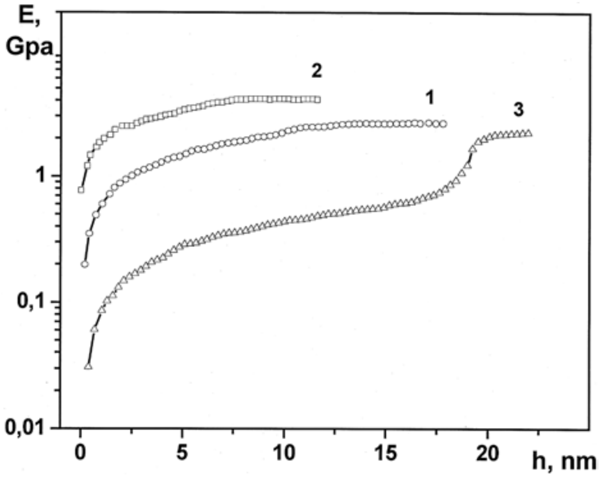

Fig. 2. The Young modulus versus indentation depth for PS (M = 270 000):
1 – untreated sample, 2 – sample annealed at 120 °C during 2.5 hours,
3 – sample UV-irradiated during 2 hours in air

We also studied the influence of different treatments on the mechanical qualities of PS (M = 270 000) surface layer. The results are shown in Fig. 2. Plot 1 corresponds to the initial untreated sample prepared as described in the Experimental section. As it is seen from the plot 2, sample annealing at 120 °C (above the bulk polymer transition temperature $T_{g,b}$) during 2.5 hours with a subsequent slow cooling down produced some increase of the elastic modulus. This effect may be explained in the following way. During such annealing the residual solvent (toluene) evaporates from the polymer (during simple drying in ambient conditions only a part of toluene evaporates before the PS structure ‘freezes’) and at the same time polymer structure relaxes to more equilibrium, close packed state. As a consequence, some hardening of polymer surface layer as well as its bulk is observed.

The comparison of plots 1 and 3 (Fig. 2) reveals that the 2-hour UV-irradiation of the initial PS sample (M = 270 000) caused a sufficient Young modulus decrease within the surface layer of 15–20 nm thickness. It is known that in the course of UV-irradiation oxidizing destruction of a polymer occurs, resulting in essential change of the chemical structure and physical state of the surface layer: rather low-molecular-weight PS compounds (the products of polymer oxidative destruction) are formed with their fraction increasing with the increase of UV-irradiation time. It should result in plastification of the PS surface layer. It is worth noting that the surface layer elastic modulus values of photoxidized PS $M = 270\ 000$ (Fig. 2, plot 3) and nonoxidized low-molecular PS $M = 8700$ (Fig. 1, plot 3) are very similar. As we have shown previously [9, 10], $T_{g,s}$ of both (photooxidised and low-molecular-weight) PS samples is lower than room temperature (20 ºC), i.e. their surface layers are not glassy even under normal ambient conditions.

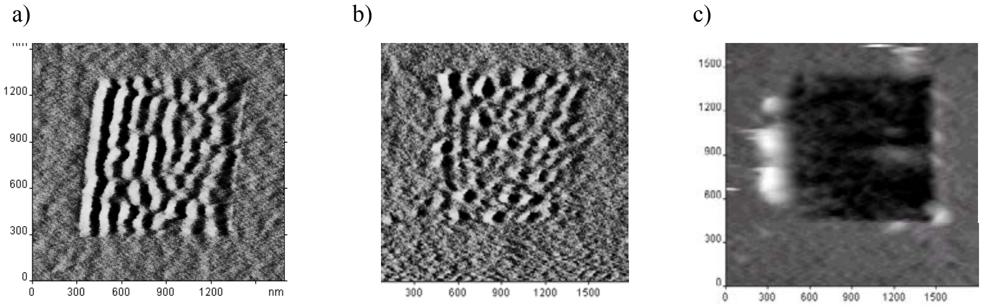

Fig. 3. AFM images ($1,7\times1,7\ \mu m^2$) of PS surface deformation caused by AFM probe; $M = 270\ 000$ (a), 50 000 (b) and 8700 (c)

In addition to the above-described nanoindentation experiments, we studied the character of PS surface deformations caused by AFM scanning (see Experimental section). These experiments can be interpreted as wearing or abrasion surface testing at nanolevel with AFM probe working as ‘nanoscraper’ under a certain loading force. The results of the comparative PS surfaces study for three different molecular weights are represented in Fig. 3. The undisturbed PS films microroughness observed using tapping mode AFM and calculated within 1×1 μm area is 0.5–1.5 nm. As is seen from Fig. 3a and b corresponding to rather high-molecular-weight PS ($M = 270\ 000$ and 50 000), the orientation ordering of the surface takes place, i.e. the formation of nanoscale bundles (or bumps) with the period of 100–150 nm and the amplitude of ~3–7 nm, oriented perpendicular to the scan direction. Such patterning on different polymer surfaces was reported earlier but still is not well-studied [1, 11]. However, this effect implies surface plastic deformation and indicates that at room temperature the PS surface layer is already in some transient state, between glassy and rubbery one.

Quite different result is seen in Fig. 3c for low-molecular-weight PS ($M = 8700$). In this case, AFM tip interaction with a surface results in the mechanical removal (scraping away) of a substance with a pit (10–20 nm depth) formation, i.e. the glassy polymer surface layer behaves as a high-viscous (wax-like) liquid.

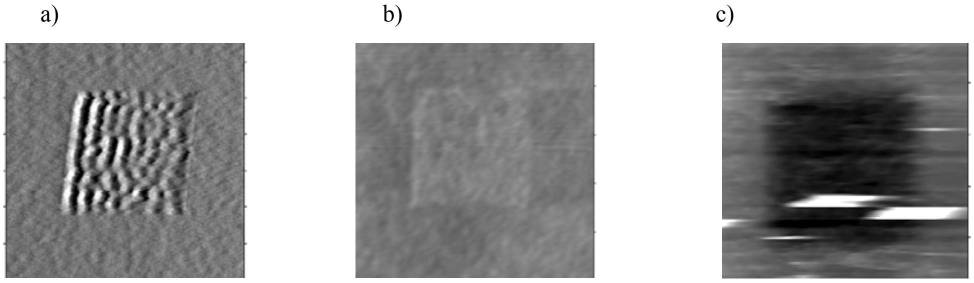

Fig. 4. AFM images (2×2 μm^2) of PS surface deformation caused by AFM probe (M = 270 000): a) untreated sample, b) sample annealed at 120 °C during 2.5 hours, c) sample UV-irradiated during 2 hours in air

Similar comparative experiments were performed with UV-irradiated, annealed and untreated PS samples with M = 270 000 (see Experimental section). AFM-image in Fig. 4b indicates that annealing procedure resulted in the more hard, wearproof PS surface (only subsequent long scanning or load increase produced oriented patterning). The character of the UV-irradiated PS surface deformation (Fig. 4c) is very similar to that observed for PS with M = 8700 (Fig. 3c): photooxidized polymer shows a liquid-like behaviour. It should be marked that this effect occurs only after a long-time irradiation (over 60–90 min).

4. Conclusions

Mechanical properties of polystyrene thin surface layers were studied by the novel methods based on atomic force microscopy. A significant difference between the bulk and surface mechanical properties was found out. We demonstrated that PS thin (~10–20 nm) near-surface layer behaves like a material exhibiting rubber elasticity (or even viscosity) than one of the glassy state. A strong dependence of the surface layer mechanical properties on the polystyrene molecular weight and different types of polymer treatment (annealing, UV-irradiation) was demonstrated. The observed correlations between PS surface layer mechanical properties and its glass transition temperature variations (studied in our previous works) prove the same origin of these phenomena.

The results of the polystyrene surface study allow us to build 'two-dimensional' nanostructures of metal particles embedded into polymer thin surface layer.

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