Determination of nanoscale mechanical properties of rubbers under uniaxial stretching by means atomic force microscopy

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Abstract

Polymers and various composites on their basis have long and successfully used in a variety of industries. Currently one of the most promising directions for further improvement of their mechanical and operational characteristics associated with different types of nanoparticles as a filler, i.e. the creation of nanostructured materials. Atomic force microscopy (AFM) is one of the most promising tools for the study of such materials internal structure. Its principal advantage is that the AFM allows to obtain information not only on the morphology of the matter structure at the nanoscale level, but also on its local physical and mechanical properties (which, as experience shows, may differ significantly from what we see at the macro level). The successful development of modern nanotechnologies in materials science is not possible without this knowledge.

Atomic force microscopy also allows to explore local strength properties of nanostructured materials. Appropriate experimental studies of the nanostructure of elastomers and elastomeric nanocomposites, pre-stretched at the macro level until prescission states were held in ICMM UB RAS. Experiments have shown that the interaction of the AFM probe with previously deformed surface differs substantially from that observed in samples unloaded. Most of the standard models used for interpretation of the results of AFM scanning, are based on the solution of the classical problem of Hertz contact between a rigid sphere and a flat linearly elastic half-space, which does not take into account the given factor.

Model studies of contact interaction between the AFM probe and the surface of uniaxially stretched polymer sample were carried out to assess emerging errors. Two types of materials have been considered: 1) neo-Hookean material; 2) real natural rubber NR0-799A (its mechanical properties were approximated by Ogden potential). Contact boundary problem on pressing of hard cone probe with a rounded tip (probe) in a nonlinearly elastic surface has been solved for this purpose. At calculations the sample was subjected to uniaxial tension before the probe indentation. Pre-stretching elongation ratio varied from 1 to 7. The problem was solved in a three-dimensional formulation, finite element method was used. As a result the dependencies between elastic

reaction force on the indenter F, the indentation depth of the AFM probe into the material u and pre-stretching elongation ratio of the sample λ_s were built.

Calculations showed that the indentation force essentially depends on the pre-stretching of the sample, with the relationship between F and λ_s is nonlinear. The more deformed polymer is the more it manifests itself. These results are planned further to use in the study of the destruction of nanostructured polymer materials with the help of atomic force microscopy.

Using advanced nanostructured materials in modern industry we need more profound knowledge of their internal structure and physical properties at micro, meso and nanolevels. Atomic force microscope (AFM) is one of the most promising tools to solve this problem [1, 2]. The force interaction between investigated surface and the cantilever beam (cantilever) with a sharp silicon probe at the free end underlies of its work. Typically, this probe (indenter) has a conical shape with rounded apex. The length of the beam is around 100–200 microns, the height of the cone is equal to 1–3 microns, tip radius (defining measurement accuracy) varies from 10 to 100 nm. Three operating modes of an atomic force microscopy are determined depending on the interaction between cantilever and sample surface: contact, non-contact and semi-contact. The greatest interest for the materials science is the contact mode (power or indentation mode) when the top of the probe is in direct contact with the surface and pressed monotonically into a specimen surface [3]. This mode allows to obtain information not only about the surface topography but also local mechanical properties at micro and nanoscale [4, 5, 6, 7], which can be very much different from the macroscopic characteristics [8].

AFM probe scans the surface of the test sample in an experiment. Obtained thereby data are the relationship between the coordinates of scanning points, the reaction force acting on the probe and the depth of indentation. These results of themselves are not sufficiently informative. Therefore the further theoretical decoding involving various physical and mechanical models is required (taking into account the various factors that affect the interaction of the probe and the surface, as well as additional knowledge about the research subject) [9, 10].

Atomic force microscopy allows you also to investigate the local strength properties of nanostructured materials. Experimental studies of the nanostructure of elastomers and elastomeric nanocomposites, pre-stretched at the macro level until prescission state, were carried out in ICMM UB RAS [11]. It was established that nanofibers (nanostrands) with mechanical properties different on characteristics of the base material can be formed in the top of the microcrack and the interaction of the AFM probe and the pre-deformed surface differs substantially from that observed in samples unloaded.

Standard software supplied to decrypt the atomic force scanning (AFM), based mainly on the models using Hertz classical solution of the contact between rigid sphere and a linearly elastic flat halfspace [12, 13]. In case of pre-loaded specimens these methods should be used with great caution for the following reasons: At first, the Hertz solution takes no account of that halfspace can be deformed previously. Secondly, the studied polymers are "soft" non-linear elastic materials, that is, an AFM probe can be pressed into the surface under study to a considerable depth (thereby the theory of finite deformations must be used).

The computer modeling of the AFM probe indentation in pre-stretched non linear elastic specimen was carried out to evaluate arising due to this errors in decoding results of AFM scanning. Mechanical response of the interaction was determined from the solution of the contact boundary value problem of pressing a hard cone with rounded apex in a soft elastic surface. Calculated scheme is shown in Fig. 1. The sample was subjected to a uniaxial pre-deformation (λ_s is the extension ratio of pre-stretching). Solution was sought by finite element method (in 3D formulation). Mechanical properties of elastomer were described by using various elastic potentials. As a result, dependences of the elastic reaction force F on mechanical properties of the sample material and geometric characteristics of the probe (tip radius R and cone angle α) were calculated. Typical values of R=10 nm and $\alpha = 40°$ for modern probes were taken in the calculations.

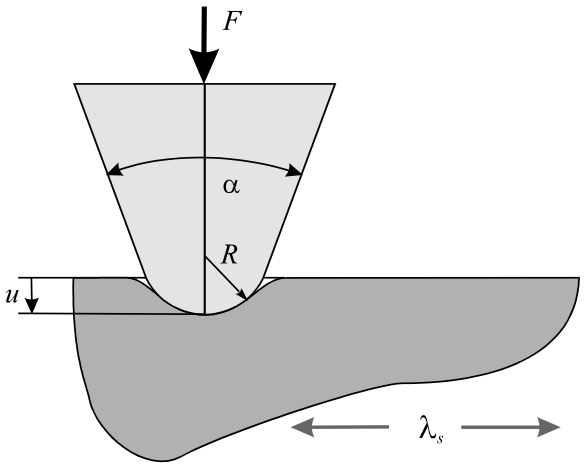

Figure 1: Calculated scheme of the model study of AFM probe indentation in pre-loaded specimen

Fig. 2 shows the dependence of $F(u, \lambda_s)$ when the mechanical properties of the polymer sample are described by neo-Hookean potential (E_s is the Young's initial modulus). Extension ratio λ_s was varied from 1 to 7 (tension) and from 1 to 0.45 (compression). The finite element mesh was composed of linear tetrahedral elements (polymer — about 250,000 elements, the probe — 25000). It was found that pre-deformation of the surface significantly affects the reaction force of the probe F for sufficiently large stretchings and not so much at small. For example, at the depth of probe indentation $u = 0.5R$ force F for $\lambda_s = 5$ increases 2.67 times compared with the case $\lambda_s = 1$, but for sample extension $\lambda_s = 2$ the increase was only 16%. Clear from the graph that the reaction force F on indentation the probe into a pre-compressed polymer with decreasing values of λ_s weakens. This can be explained by the fact that uniaxial compression of the body (e.g., a cube) with free lateral boundaries is equivalent to biaxially stretched on other faces. That is, pressing at $\lambda_s < 1$ is equivalent to the case of indentation into material, stretched along mutually perpendicular directions.

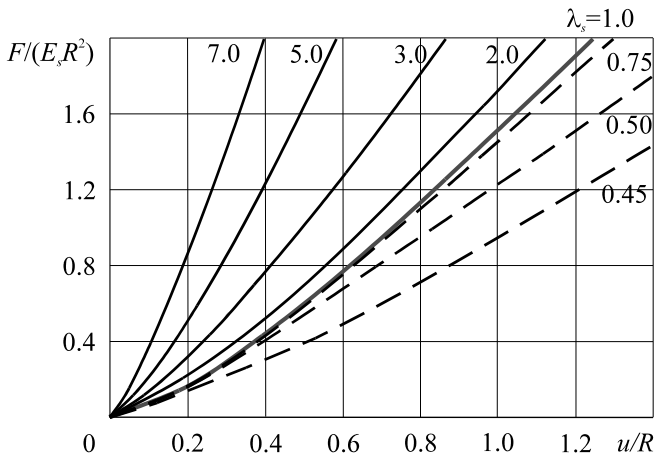

Figure 2: The interaction of the AFM probe with uniaxially deformed polymer sample (neo-Hooke). Solid lines — stretching, dashed lines — compression

Similar model studies were also carried out for the real elastomer (natural rubber NR0-799). As before, the contact boundary value problem of the AFM probe indentation in the polymer was solved using finite element method (in 3D setting). The finite element mesh composed of the same linear tetrahedral elements was similar to the previous neo-Hookean version.

Mechanical macro uniaxial tensile test (sevenfold elongation of the sample) was carried out to determine the elastic properties of this rubber. The resulting strain curves were approximated by Ogden potential of the 2nd order ($N = 2$) [14, 15]. Approximation error was less than 2%.

$$w_{Ogden} = \sum_{i=1}^{N} \frac{2\mu_i}{\alpha_i^2} \left(\bar{\lambda}_1^{\alpha_i} + \bar{\lambda}_2^{\alpha_i} + \bar{\lambda}_3^{\alpha_i} - 3\right) + \sum_{i=1}^{N} \frac{1}{D_i} \left(J^{el} - 1\right)^{2i},$$

where $J^{el} = \lambda_1\lambda_2\lambda_3$, $\bar{\lambda}_n = J^{-1/3}\lambda_n$ are deviators of principal extensions λ_n. D_i are material parameters responsible for the thermal expansion. The initial shear modulus μ_0, bulk modulus K_0, as well as the initial Young's modulus E_0 and Poisson's ratio ν_0 (for the sample $\mu_s = \mu_0$, $K_s = K_0$, $E_s = E_0$, $\nu_= \nu_0$) are expressed through the parameters of Ogden potential as

$$\mu_s = \sum_{i=1}^{N} \mu_i, \quad K_s = \frac{2}{D_1}, \quad E_s = \frac{9K_s\mu_s}{3K_s + \mu_s}, \quad \nu_s = \frac{3K_s - 2\mu_s}{6K_s + 2\mu_s}.$$

The depedence of nominal stess σ^0 on the sample extention ratio λ in uniaxial tension is shown in Fig. 3. The values of Ogden potential parameters were determined from this curve. They are given in Table 1.

Table 1. Parameters of Ogden elastic potential for natural rubber NR0-799A

$i = 1, N$	μ_i, MPa	α_i	D_i, MPa^{-1}
1	+7.269567E-17	+7.28334893	5.3885E-1
2	+7.473002E-2	-3.19357443	0.0

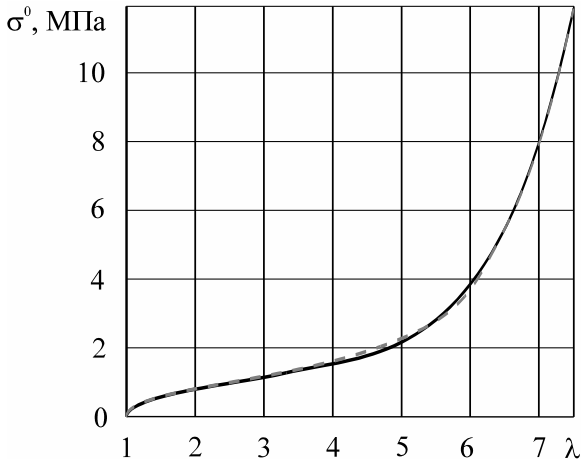

Figure 3: Approximation of the real stress–strain dependence (dashed line) for natural rubber NR0-799A by means Ogden potential (solid line)

Fig. 4 shows dependences of the reaction force on the probe F on the indentation depth u in the pre-stretched samples of natural rubber NR0-799A. The pre-stretched extension ratio λ_s has ranged from 1 to 7.

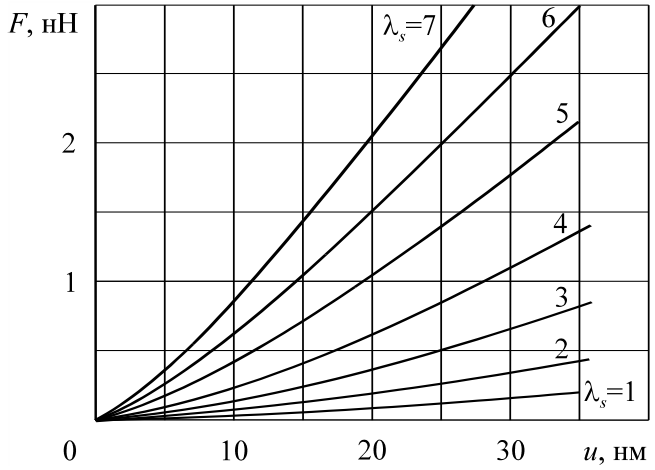

Figure 4: Model dependences of the force pressing an AFM probe into a sample of the natural NR0-799A rubber on the indentation depth u and pre-stretched extension ratio λ_s

Comparing these results with the neo-Hookean material showed that in natural rubber the pre-stretching of material considerably stronger effect on the process of probe indentation. For example, in case of λ_s=7, and u=20 nm in the reaction force F for natural rubber increases almost by 30 times as compared to not pre-stretched sample, whereas for neo-Hookean material the increase is about 6 times. That is to say this factor affects the process of AFM probe indentation and consequently the determination of material nanoscale elastic characteristics very essentially.

Obtained dependences are planned to be used in 2016 for the correct interpretation of the results of AFM scanning pre-stretched real natural rubber, i.e. in studying the processes of its destruction at nano and micro levels.

Acknowledgements

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