Computer modeling of the interaction between AFM probe and nano-strands arising in the polymer at its destruction

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Abstract

Atomic force microscopy (AFM) is one of the most promising instruments of investigation materials at the nanoscopic level. You can use it to study not only the topology of the internal structure of materials, but also their local physical properties which, as experience shows, can be substantially different from what we see at the macro level.

Standard software supplied for the interpretation of the results of scanning atomic force, mainly based on models using the classical solution of the Hertz contact a rigid sphere and a plane linear elastic half-space. This is sufficient in most cases. However, there are situations when the Hertz solution should be used with great caution. This work is devoted to theoretical investigation of such cases, namely — contact AFM probe and nanostrand as long nonlinear elastic fiber.

Experimental studies of the nanostructure of elastomers and elastomeric nanocomposites in prescission state were conducted in ICMM UB RAS. It is established that, nanowire strands with mechanical properties different of the base material formed in the apex of microfracture in stretched sample.

The calculation of the elastic modulus strands by standard methods in this case gives great mistake, as contact between the probe and the surface does not occur the normal and material is nonlinear elastic. To estimate arising from this error, the following modeling studies were carried out.

Contact boundary value problem of pressing the AFM probe in free hanging nonlinear elastic nano strand as a long horizontal cylinder with a rigid cantilevered at the ends was solved. Length and diameter of the strand were taken in accordance with the real experimental data. Solution sought in three-dimensional formulation finite element method. It was believed that the probe affects the strand perpendicular to its axis. As a result, the dependencies between the elastic reaction force on the indenter F, indentation depth probe into the material u, the distance from the end of the strand L and the magnitude of the nanofiber deflection in contact cross section d_z. It was found that value of d_z far exceed the u. In cases where an AFM probe impacted strand is not in the axial plane, the there was a significant shift of the nanostrand in lateral direction, and the direct embedment depth was less.

Atomic force microscopy (AFM) is one of the most promising research tool of materials at the nanoscopic level [1, 2, 3, 4]. Invented in 1982 scanning atomic force microscope [5] (Nobel Prize in Physics in 1986) is widely used in various fields of modern science — physics, chemistry, biology, etc. AFM is successfully used in materials science in the study of the morphology and local physical and mechanical properties of the material at the nanoscopic level, which, as experience shows, can be very much different from the macroscopic characteristics.

Local elastic modulus [1, 6], hardening parameters [7], creep [8] is possible to determine by AFM. Atomic force microscope allows you to observe micro-processes such as the appearance of dislocations, the occurrence of shear instability, phase transitions, and many other phenomena previously unavailable to conventional techniques [9].

The steel cantilever beam with a silicon probe at the free end is the main element of an atomic force microscope. Typically this probe (indentor) has a conical shape with rounded apex. Beam length is about 100–200 microns, cone height of 1–3 microns. Probe tip radius (which determines the instrument resolution) in modern cantilevers varies from 10 to 50 nm.

There are three operating modes of an atomic force microscope depending on the nature of the force between the cantilever and the sample surface: contact (contact mode), contactless (non-contact mode), semi-contact (semi-contact mode or tapping mode). In the present paper only contact mode considered when the probe tip is in direct contact with the surface (power mode) and is pressed monotone into a specimen. This mode allows to receive information about the relief as well as on the local physical and mechanical properties of the material [4, 10, 11].

This method is particularly well suited for the study of polymeric materials: As a rule, an AFM probe is made of much more rigid materials, which allows considering it practically non-deformable in comparison with the polymer. The indentation hard probe into the soft polymer surface to a considerable depth allows building the relationship between the reaction force and indentation depth (both on the direct and reverse cantilever motion). With this information, you can explore the local nonlinear elastic, elastoplastic and viscoelastic properties of the material. But it needs its theoretical decoding engages a diverse range of physical and mechanical models (taking into account different factors affecting the interaction between the probe and the surface, as well as additional knowledge about the subject of research) [12, 13, 14].

Standard software supplied to decrypt the atomic force scanning (AFM), based mainly on the models using a classical solution of the Hertz contact of two linearly elastic spheres (or a sphere and a flat half, if one of them has infinite radius). In most cases this is enough. However, there are situations where the Hertz solution should be used with great caution. For example: 1) a very "soft" materials, when an AFM probe falls into the sample to a great depth, and 2) the probe and material contact not along the normal, but at an angle, and 3) the object of study can be displaced as a rigid body (shift) at influence on it of an AFM probe. This work is devoted to the theoretical study of last version.

Experimental studies of the nanostructure of elastomers and elastomeric nanocomposites in a prescission state were carried out in ICMM UB RAS in 2011–2012 [15, 16]. Isoprene rubbers with nanofiller of carbon black particles were tested. AFM study of microscopic crack tips of the stretched samples showed that nanofibers–strands with mechanical properties different of the base material formed there. Usually they are oriented in a perpendicular direction to the direction of the gap and have the characteristic average diameter and fiber length of about 80 nm and 800–1000 nm, respectively.

Decoding obtained by AFM scanning experimental data using the now-standard Deryagin-Muller-Toropov model (DMT) [17, 18], (Hertz solution + additional term, taking into account the adhesive interaction of the probe with the surface) showed that the stiffness of the nano-fibers approximately three times higher than the rest matrix. This can be explained by the fact that the polymer in nano-strands is in highly oriented state. But then — as shown by reported in the literature evaluation [19] stiffness should be even higher, and much more. The problem is compounded by the fact that based on the solution of the Hertz model assumes DMT interaction of the probe with a flat surface only in the perpendicular direction. It is clear that this condition in the case of contact with strand is not performed. Also in contact with nano strand bending is possible, that is the deflection of cantilever and the indentation depth of the probe apex (the modulus of material which is calculated using this value) in this case is not the same thing. Consequently, the standard DMT technique is to give a big mistake. The following theoretical studies were conducted to assess it.

Contact boundary value problem of pressing of an AFM probe into free hanging (unstretched) nonlinear elastic nano-strand as a long horizontal cylinder with rigidly fixed at the ends was solved. The strand length and radius were taken in accordance with the actual experimental data: $L_s = 1000$ nm, $R_s = 40$ nm. It was considered that nano-strand consists of incompressible nonlinear elastic material, which mechanical properties are described by Neo-Hookean potential. It was also assumed that the medium is homogeneous and isotropic, i.e. it has no oriented molecular chains and filler particles. Initial Young's modulus E_s was taken to be 1 MPa, which corresponds to 10^{-3} nN/nm^2. AFM probe was represented as a rigid cone with rounded apex. Rounding radius of apex $R = 10$ nm, cone angle $\alpha = 40°$.

Solution were looking for in three-dimensional formulation. Finite element method was used. Mesh size of tetrahedral elements with linear approximation of displacements was averaging 800,000 (strand) and 100000 (indenter). The calculation scheme is shown in Fig. 1.

It was considered that the AFM probe acts on the strand downwards perpendicularly to its axis, wherein the horizontal displacement of the probe u_y from vertical plane passing through the initial strand axial line is constant. As a result, dependencies between the elastic reaction force on the indenter F, the probe depth of indentation into polymer u, the distance from the strand end L full vertical AFM probe displacement u_z were built. Dependences of F on u and u_z for the case where $u_y = 0$ are shown in Fig. 2. Fig. 3 illustrates the resultant picture of strand bending.

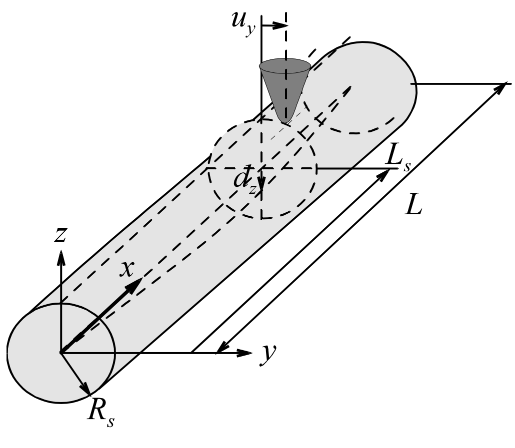

Figure 1: Calculation scheme of the problem of contact between an AFM probe and a nano-strand

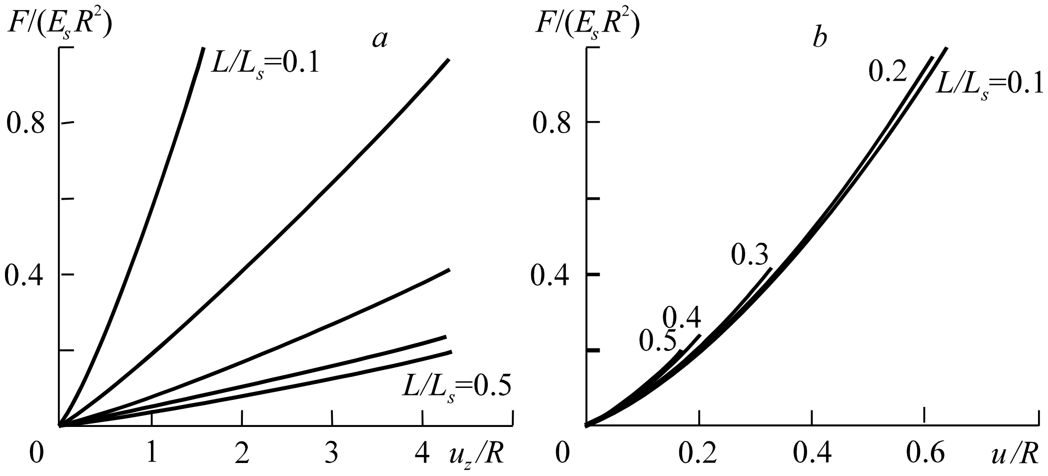

Figure 2: Dependence of reaction force F on u_z (a) and u (b) for the case $u_y = 0$

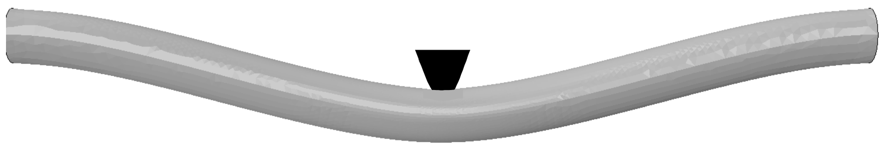

Figure 3: The AFM probe indentation into nanostrand ($u_y = 0$)

It was found that the values of u_z far exceed u. Thus, when the probe is pressed into the strand middle ($L/L_s = 0.5$) in a plane passing through its axis, the depth of indentation (u) is only a few percent of the total nano-fiber bending. Relevant dependences of u on u_z are shown in Fig. 4.

If the AFM probe was indented into the strand not in axial plane ($u_y \neq 0$) the depth of indentation u was even less than in case $u_y = 0$. Dependence of strand axis lateral shear d_y on vertical probe displacement u_z for the case of $u_y = 0.5R$, $L/L_s = 0.5$ is shown in Fig. 5. In fact, the repulsion of strand to side instead of the probe indentation into surface occurs.

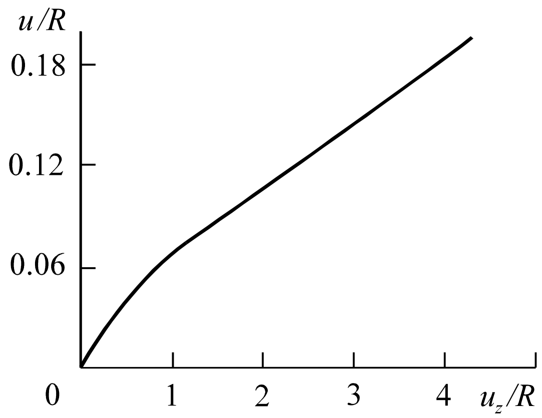

Figure 4: Dependence of AFM probe depth indentation into nano-strand u on the total vertical displacement of indenter u_z (case $u_y = 0$)

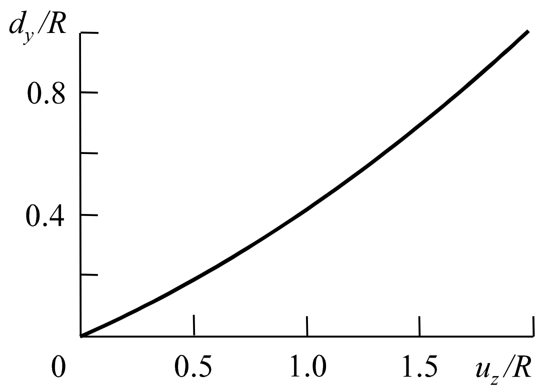

Figure 5: Dependence of nano-strand axis lateral shear d_y on the indenter total vertical displacement u_z for the case $u_y = 0.5R$, $L/L_s = 0.5$

Hence we can conclude that the problem of the interaction between AFM probe and polymer nano-strand requires a careful and thorough research. Standard methods of atomic force microscopy in this case need considerable refinement. It is planned to carry out research for pre-stretched strand (which is quite probable for sliding microcrack edges, where it was formed), as well as to consider the case when it is not hanging freely in space but lies on a rigid surface.

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References

[1] Bhushan B. Handbook of micro-mano-tribology. Springer, 1999, 433 p.

[2] Golovin Yu.I. Introduction to nanotechnology. Moscow, 2003, 112 p. (in Russian)

[3] Bhushan B. Nanotribology and nanomechanics. Springer, 2005, 1148 p.

[4] Mironov V.L. Fundamentals of the scanning probe microscopy. Nizhnij Novgorod, 2004, 115 p. (in Russian)

[5] Binnig G., Rohrer H., Gerber C., Weibel E. Surface studies by scanning tunneling microscopy. Phys. Rev. Lett., 1982, V. 49, N 1, P. 57–61.

[6] Vanlandingham M.R., McKnicht S.H., Palmese G.R., Eduljee R.F., Gillepie J.W., McCulough Jr.R.L. Relating elastic modulus to indentation response using atomic force microscopy // Journal of Materials Science Letters, 1997, V. 16, P. 117–119.

[7] Dao M., Chollacoop N., Van Vliet K.J., Venkatesh T.A., Suresh S. Computational modeling of the forward and reverse problems in instrumented indentation // Acta Mater., 2001, V. 49, B. 19. P. 3899–3918.

[8] Fischer-Cripps A.C. Nanoindentation and indentation measurements // Mater. Sci. Eng., 2004, V. 44. P. 91–102.

[9] Fischer-Cripps A.C. Nanoindentation. Springer, 2002, 217 p.

[10] Wiesendanger R. Scanning Probe Microscopy and Spectroscopy. Cambridge Universtiy Press, Cambridge, 1994, 637 p.

[11] F. Giessibl, Advances in Atomic Force Microscopy. // Reviews of Modern Physics, 2003, V. 75, N 3, P. 949–83.

[12] Garishin O.K. Simulation of atomic-force microscope contact mode operating taking into account nonmechanical forces of interaction with a specimen surface // Computational continuum mechanics, 2012, V. 5, N 1, P. 61–69.

[13] Garishin O.K., Lebedev S.N. Modeling of contact between atomic force microscope probe and an elastic brittle damage material // XL Summer school "Advanced problems in mechanics": Proceedings, St.-Petersburg, 2012, P. 117–122.

[14] Garishin O.K., Lebedev S.N. Atomic force microscopy as applied to materials with anisotropic nanostructure // XLI Summer school "Advanced problems in mechanics": Proceedings, St.-Petersburg, 2013, P. 225–230. (in Russian)

[15] Morozov I.A., Solod'ko V.N. Study areas of cracks in rubber vulcanizates by atomic force microscopy // Vestnik Permskogo universiteta. Seria Fizika. Perm, 2012, N 4(22), P. 158–165. (in Russian)

[16] Morozov I.A., Lauke B., Heinrich G. AFM investigation of structure and mechanical properties of crack zones in CB filled/unfilled vulcanizates // Kautschuk Gummi Kunststoffe, 2013, N. 10. P. 71–76.

[17] Derjaguin B.V., Muller V.M., Toropov Yu.P. Effect of contact deformations on the adhesion of particles. // J. Colloid. Interface Sci., 1975, V. 53, N 2, P. 314–326.

[18] Deryagin B.V., Churaev N.V., Muller V.M. The surface forces. Moscow, 1985, 398 p. (in Russian)

[19] Svistkov A.L., Lauke B. Differential constitutive equations of incompressible media at finite deformations. Prikladnaya mexanika i texnicheskaya fizika — Applied Mechanics and Technical Physics, 2009, V. 50, P. 158–170.

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