Surface Force Spectroscopy of Elastomeric Nanoscale Films

Sergei A. Chizhik [1], Valery V. Gorbunov [1,2], Igor Luzinov [3], Nobi Fuchigami [2], Vladimir V. Tsukruk [2*]

[1] Metal-Polymer Institute, National Academy of Sciences, Gomel, Belarus
[2] Department of Materials Science & Engineering, Iowa State University, Ames, Iowa 50011, USA
[3] School of Textiles, Fiber and Polymer Science, Clemson University, Clemson, South Carolina 29634, USA

SUMMARY: We studied nanomechanical properties for a series of ultrathin films of elastomeric materials from polyisoprene rubbers and tri-block styrene-butadiene-styrene copolymer, SEBS. As we observed, the Hertzian approximation for elastic mechanical deformation of double layer films can be used for the analysis of force-distance data at modest indentation depths and film thickness higher than 3 nm. For thinner films, the influence of solid substrate becomes very significant. On the other hand, the applicability of the Hertzian approximation is limited by the rate dependent elastomeric deformation. We demonstrated that Johnson modification of the contact mechanics model that includes a viscoelastic contribution could be utilized to obtain reasonable fitting of loading data for elastomeric materials.

Introduction

Ultrathin polymer coatings are important for many fine applications with severe space limitations such as microelectromechanical systems or high resolution photolithography. [1)] Fabrication of robust polymer coatings with thickness well below the size of the macromolecular coils (<10 nm for typical molecular weights) is a challenge problem. Moreover, testing of their surface properties, especially, nanomechanical and tribological behavior, is a non-trivial procedure. In this contribution, we demonstrate several examples of nanomechanical probing of a series

* To whom correspondence should be addressed: vladimir@iastate.edu

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of ultrathin compliant elastomeric polymer films with elastic modulus ranging from 2 MPa to 400 MPa and thickness ranging from 2 nm to 400 nm deposited on solid substrates.

Experimental

As model systems, we used polyisoprene (PI) rubber (Aldrich) with molecular weight M_w = 800,000. Styrene-butadiene-styrene block copolymer (SEBS) was Kraton (Shell) with 29% of styrene block and M_n = 41, 000. Polymer films of different thicknesses were spin-coated on atomically flat silicon wafers. Thickness of the films was controlled with an ellipsometer. Ellipsometry was performed with a COMPEL automatic ellipsometer (InOmTech, Inc.). The angle of incidence used was 70°. All reported thickness values were averaged over six measurements.

Scanning probe microscopy (SPM) studies were performed on a Dimension 3000 microscope (Digital Instruments, Inc.) according to the procedure described earlier [2)]. Force-distance data were collected with silicon cantilevers with spring constants in the range of 2 – 100 N/m with approaching-retracting probing frequency in the range of 0.1 – 10 Hz. Calibration of spring constants was done from the resonance frequency shift and tip radii were measured by using tethered gold nanoparticles as described before. [3,4)] To satisfy conditions for elastic mechanical contact, we selected relatively blunt tips with radius in the range of 60-70 nm. Then, to conduct data processing, we assumed that polymer layers can be represented by a uniform layer with "effective" elastic modulus, *E*. Indentation depth – mechanical load curves were calculated from the experimental force-distance data by using calculation routines derived from a two spring model as described in detail in previous publications. [5,6)]

To obtain multiple force-distance data, we performed force-volume measurements for selected surface areas and collected 64 or 256 force-distance curves for areas 1 x 1 μm.[7)] Then, we selected at least 10 curves without instabilities and artifacts with "most

probable" shape from histogram distributions and conducted their complete analysis. Analysis of histograms of surface distribution of nanomechanical response shows that standard deviation for the data presented here is in the range of 30% within selected surface area.

Results and discussion

Fig. 1*a* demonstrates typical force-distance curve for the rubber film with 200 nm thickness. It shows the initial elastic deformation as a result of a jump-in contact (point A), a long range of very gradual upward cantilever deflection caused by low mechanical resistance of compliant rubber film (segment A-B), followed by a sharp increase in the slope at indentation depths when tip starts "feeling" the solid substrate (Point B). In fact, elastic modulus of silicon is 160 GPa that is three to six orders of magnitude higher than for elastomers. Correspondingly, penetration versus mechanical

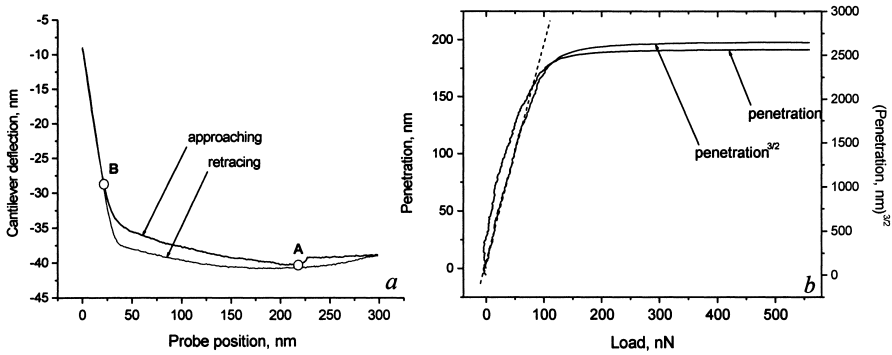

Fig. 1. Force distance data for the 200 nm rubber film (a) and corresponding penetration-load curve (b). A straight dash line shows linear approximation that can be used for elastic modulus calculation within the Hertzian model.

load curve calculated from force-distance data shows very fast deformation for low mechanical loads (less than 10 nN) followed by "saturation" at higher loads (Fig. 1*b*).

To calculate the elastic modulus value from the penetration-load data, we can use either a linear approximation of the data in the Hertzian coordinates (penetration$^{3/2}$ ~ mechanical load) (Fig. 1b) or direct fitting of the experimental data with the appropriate mechanical model (for example see Fig. 2). Significant deviations from the Hertzian behavior were observed for the penetrations higher than 60% of the total film thickness. Therefore, for more detailed analysis of thinner films, we used elastic deformation range less than 50% of the total film thickness.

In addition to conventional Hertzian approach, data for the thin rubber films with thickness of 10 - 200 nm were analyzed with the double-layer contact mechanics model [7] (Fig. 2). This model considers cooperative deformation of two layers with different elastic moduli within Hertzian approximation. We adapted this model to describe compliant polymer layer on top of stiff solid substrate. The main equation of this fitting is the equation for indentor-surface contact radius, a, in the form:

$$\frac{a}{a_{Hertz}} = \left[\frac{J^{\frac{4}{3}} + 0.8 \cdot t/a_{Hertz}}{\sqrt{1 + \left(0.8 \cdot t/a_{Hertz}\right)^2}} \right]^{\frac{1}{4}},$$

where a_{Hertz} is the contact radius calculated correspondingly to the Hertzian theory; $J = \frac{E_1}{E_2} \cdot \frac{1-\nu_2^2}{1-\nu_1^2}$; E_1, ν_1, E_2, ν_2 are Young's modulus and the Poisson ratio for compliant polymer layer with thickness t and hard substrate, correspondingly.

The elastic modulus value determined from these fittings varies in the range from 0.4 MPa to 4.5 MPa depending upon film thickness. These values are scattered around bulk value of 1.9 MPa measured for this rubber material with standard tensile stress routine.[6] Typical penetration depths were in the range of 12 – 40 nm for normal loads from 3 to 20 nN and the mechanical contact area was estimated to be within 5 – 10 nm.

As we observed, reasonable results can be obtained by using the double layer approximation for elastomeric films with thickness higher than 3 nm. For thinner films, the range of unambiguous nanomechanical readings is limited by both initial uncontrolled elastic deformation due to the jump-in contact (low loads) and a solid substrate contribution (high loads). No meaningful results can be obtained for films with thickness below 3 nm under given experimental conditions. For these films, more complicated approaches such as lateral modulation or a gradient model should be used for data analysis. [9)]

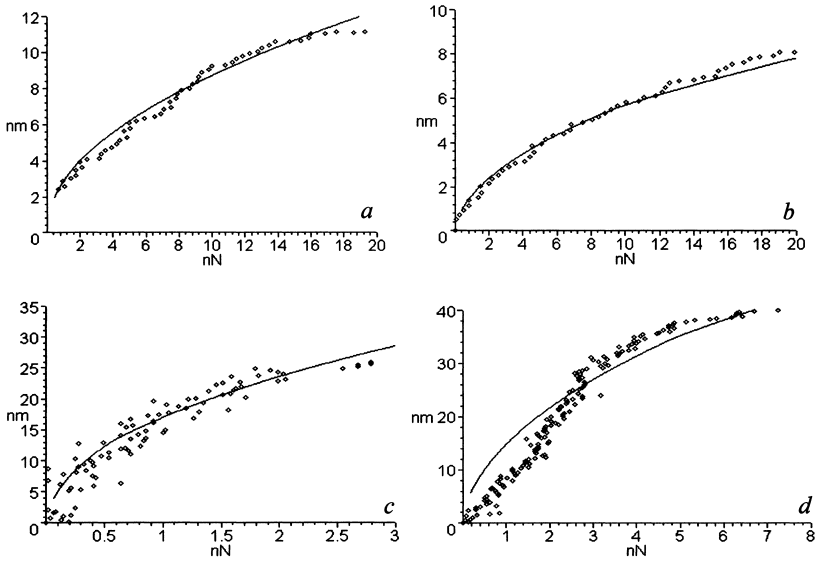

Fig.2 Penetration-load data for the PI rubber films with thickness of 11.5 nm (a), 20.3 nm (b), 31 nm (c), and 50 nm (d) with their double layer approximations (solid lines).

For the SEBS films, we compare the loading data obtained for the ultrathin films and for bulk materials (Fig. 3). As clear from this figure, for the 8 nm film, total deformation is limited by the solid substrate and resulting "saturation" occurs at mechanical loads higher than 40 nN. On the other hand, deformation for the bulk SEBS material without supporting stiff surface progresses much faster than can be

expected from the elastic Hertzian behavior (Fig. 3). The best fit in this case can be obtained for the value of elastic modulus of 140 MPa but significant positive deviation at higher indentation depths and longer probing times show significant contribution of viscous component.

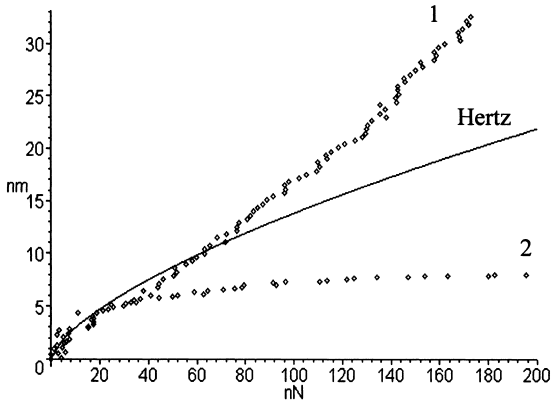

Fig. 3. Penetration-load data for SEBS bulk material (1) and the 8 nm film (2) along with Hertzian approximation for E = 140 MPa (solid line).

To analyze this rate-dependent behavior, we applied Johnson suggestion for the relationship between contact area, a, load, P, and loading time, t, for viscoelastic solids contact in the form [10]:

$$a^3(\tau) = \frac{3RUT}{4E_\infty^*}[\tau - (1-k)(1-\exp(-\tau))],$$

where $\tau = t/T$ is the reduced time, $k = E_\infty^*/E_0^*$ is the reduced modulus with E_o being initial, instantaneous modulus and E_∞ being "equilibrium" relaxed modulus for infinitely slow load, $U = P/t$ is the rate of loading, R is tip radius of curvature, and T is the relaxation time of material. This relationship was derived for a three-parameter linear viscoelastic model [10]. The local penetration depth, h, was calculated from the Hertzian approximation:

$$h = \frac{a^2}{R}.$$

By varying two primary variables, E_o and T, one can do fitting the experimental data (Fig. 4). As was observed, introduction of viscoelastic contribution can principally change the shape of penetration curve from convex to concave. The latest shape is, indeed, observed for SEBS material (Fig. 4).

The viscoelastic Johnson model produces conventional Hertzian shape for penetration-load plots in the limit of a very high rate of data collection (very short interaction time between the tip and the surface) or very fast relaxation times (Fig.4).

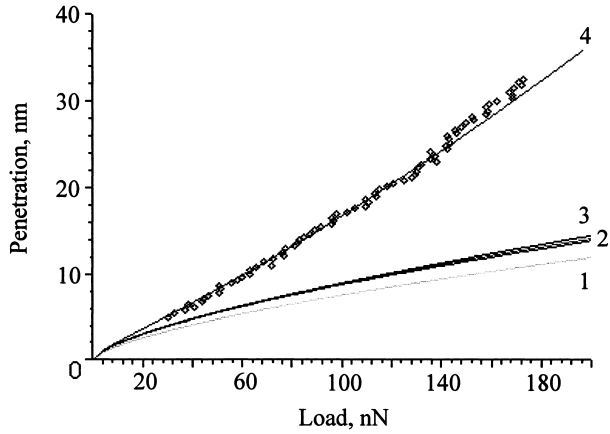

Fig. 4. Penetration-load data for bulk SEBS material (squares) and simulations (solid lines) for: 1- Hertzian model; 2, 3 – a viscoelastic model JKR model with 50 ms and 100 ms probing time, 4- the viscoelastic model with the best fit to the experimental data for SEBS bulk material.

For the thick SEBS film at room temperature (second glass transition temperature is close to 70°C), we obtain the best fit for instantaneous storage modulus of 360 MPa and relaxation time $T = 5$ ms (Fig.4).

Conclusions

In conclusion, we demonstrated that force-distance nanomechanical probing in conjunction with double-layer elastic contact mechanics model can be used for the evaluation of elastic moduli for ultrathin elastomeric films deposited on solid substrates with thickness as small as 3 nm. Viscoelastic contribution can modify nanomechanical response and can be treated within linear viscoelastic model adapted for contact mechanics.

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