Nanomechanical testing of multilayered polymer films

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Nanomechanical testing of multilayered polymer films

by

Hennady Petrovich Shulha

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
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This is to certify that the master's thesis of

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has met the thesis requirements of Iowa State University

Signatures have been redacted for privacy
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ABSTRACT

Measuring mechanical property is important in different scientific areas related to applications in macro, micro, and nanoscale devices. But unlike the microscopic measurements where numerous models are developed and tested, only a relatively very few approaches were tested nanoscale measurements. A special case includes indentation experiments for thin multilayered polymer systems. In this work, a model that describes the process of indentation in multilayered films with dimensions of several tens of a nanometer is developed and implemented in a software package. The software package is designed to work directly with files from atomic force microscopy data collected in Force Volume mode. The routine for the nanomechanical measurements of different multilayered polymer films was developed and it was shown that it is possible to receive reliable elastic modulus values and profiles. The model was tested for single hyperbranched molecules and polymer brushes, and model properties were investigated. It was found that in addition to elastic moduli behavior prediction, the model gives some estimation of the width of interfacial zone between adjacent layers.
CHAPTER 1

ELASTIC BEHAVIOR OF MULTILAYERED POLYMER SYSTEMS

1.1 Different polymeric systems and Atomic force microscopy (AFM)

The ability to probe surface properties with nanometer-scale lateral and vertical resolution is critical for many emerging applications. An important element is nanoscale (1-100 nm) compliant coating for microelectromechanical and microfluidic devices where nanoscale details of surface deformations and shearing play a critical role in overall performance. Usually, a nanomechanical probing experiment exploits either atomic force microscopy (AFM) or microindentation techniques. The utilization of conventional microindentation technique for systems consisting of compliant (elastic modulus ranging below 1,000 MPa) and ultrathin (thickness below 100 nm) polymer coatings faces critical challenges associated with uncontrolled initial indentation, which can easily span the entire thickness of nanoscale coatings and limits lateral resolution to hundreds of nanometers. Despite numerous technical issues associated with the AFM nanoprobing (e.g., non-axial loading, jump-into contact, high local pressure, and topographical contributions), a number of successful applications have been recently demonstrated.

These include nanomechanical probing of spin-coated and cast polymer films, organic lubricants, self-assembled monolayers, polymer brushes, biological tissues, and individual tethered macromolecules. Absolute values of the elastic modulus have been measured for polymer surfaces in the range from 0.01 MPa to 30,000 MPa. These measurements were conducted in a wide range of temperatures and probing frequencies, for compliant films with thickness down to 2 nm, and with vertical and lateral resolution as low as 1 and 10 nm, respectively. Elastic moduli (loss and storage), surface glass transition temperatures, and relaxation times all have been obtained with reasonable confidence by applying direct dc or ac force-distance measurements and/or cantilever modulated (vertically as well as laterally) modes. Spatial (vertical and lateral) resolution on a nanometer scale unachievable by any other probing technique makes AFM nanomechanical probing a
unique experimental tool. A further expansion of the AFM-based probing especially for ultrathin (below 100 nm) polymer films in a contact mode regime will rely on solving several fundamental issues including the evaluation of substrate effect and the elastic response for multilayered coatings. It will be shown how known approaches developed for the analysis of microindentation experiments of the elastic layered solids can be adapted to AFM experiments. Elastic moduli obtained for polymeric layers through new approaches can be compared with bulk materials to evaluate behavior and changing of properties in compliant films.

Another important application of a multilayered system is the nanomechanical study of single molecules. An understanding of the nanomechanical properties of individual organic and polymeric molecules, and their molecular aggregates at solid surfaces, is critical for the design of electromechanical and fluidic nanodevices with nanoscale contact interactions. Direct measurements of elastic properties of individual organic molecules are possible only with AFM. However, current studies are mainly limited to qualitative visualization of the surface stiffness distribution. An AFM-based pull-off mode is frequently applied to conduct analysis of tensile properties of long-chain molecules and the strength of binding interactions. Under optimal probing conditions, an application of the contact mechanics model to the compression mode could produce a reliable value of the elastic modulus, surface distribution of surface stiffness of elasticity, and even the depth profile of the elastic modulus. This approach is applicable to molecularly thick compliant films, nanoscale colloidal particles, and nanoparticulate molecules and can provide reliable information with lateral resolution below 5 nm and vertical resolution below 0.2 nm. The main disadvantage of this model regards to ultrathin compliant coatings is that the influence of substrate is strong that it is necessary to apply different theoretical models to describe the nanoindentation process and predict substrate contribution into the numerical values that can be obtained.

1.2 Models for indentation experiments

AFM is capable to do indentation experiments in several modes. The first mode includes measurements of so called Force-Distance curves (FDC). FDC contains data and relationship
between probe position and cantilever deflection (Figure 1). Microindentor (tip) is attached to the end of cantilever. During the experiment the probe is moved up and down using the deflection as feedback and FDC data is collected. Along with a single FDC curve collection there is more advanced, so-called Force Volume (FV) mode. In this mode an array of FDC data is collected and represented as a single picture. Processing of this file allows creation of distribution of FDCs (and data from FDCs) with surface and establishing correlation between elastic data from FDCs and morphology. To receive the data it is necessary to apply correct model that is able to describe the shape of the tip and process of tip penetration into the surface.

\[
\text{Deflection} \quad \text{Penetration}
\]

\[
\text{Figure 1: Left: schematic representation of tip indentation; right: Hertz (Sneddon) model of tip-surface interaction.}\quad ^{47}
\]

General relationships between the normal load and the elastic indentation are suggested in classical Hertzian and Sneddon theories, with more complex cases analyzed with the Johnson-Kendal-Roberts (JKR) approach as described in original papers and books.\textsuperscript{26,27,28,29,30} As considered, indentation depth is a function of the applied force (normal load) \( P \), tip geometry (radius \( R \) or parabolic focus distance \( c \)), as well as the mechanical and the adhesion properties of the contacting bodies. The normal load for AFM nanomechanical
probing experiments is calculated as \( P = k_n \cdot z_{\text{def}} \), where \( k_n \) is the vertical spring constant of the cantilever deflected in vertical direction by \( z_{\text{def}} \). A non-axial displacement of the AFM cantilevers caused by their tilted orientation does not usually exceed 5-10% and, thus, will be neglected here. The above mentioned \( R \) (or \( c \)) and \( k_n \) are initial system parameters, which must be measured and calibrated before the nanomechanical analysis. The Poisson’s ratio, \( \nu \), is used as well as a material parameter and is usually assumed to be known and taken as a bulk value with possible deviations playing a minor role as was already demonstrated for microindentation experiments.\(^{19}\)

As suggested in contact mechanics studies, the most general relationship between indentation depth, \( h \), and normal load, \( P \), in the course of indentation experiment can be presented in the very general form as: \(^{26-30}\)

\[
P = a h^b
\]

(1)

where \( a \) and \( b \) are specific, model-dependent geometrical parameters (e.g., \( b = 3/2 \) for both Hertzian and parabolic Sneddon’s contacts)(Figure 1).\(^{29}\)

On the other hand, the Sneddon’s model suggests a specific and practical analytical relationship between the surface stiffness, \( dP/dh \) and Young’s modulus, \( E' \), in the form:

\[
\frac{dP}{dh} = \frac{2\sqrt{A}}{\sqrt{\pi}} E'
\]

(2)

where \( E' \) is the composite modulus. As known, the composite elastic modulus is defined as follows \(^{30}\):

\[
\frac{1}{E'} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}
\]

(3)
where $E_1$ and $E_2$ are the elastic moduli of a surface and an indentor (tip).

From $dP/dh$ dependence obtained from microindentation experiment and the calculated/measured contact area variation for a specific shape of the indentor (specific analytical expressions are suggested for circular, pyramidal, and parabolic shapes), one can evaluate an absolute value of the elastic modulus. For a routine estimation of the elastic modulus value for small indentation depths, the Hertzian model of a sphere-plane contact type is applied. For larger indentations, the Sneddon’s model with a parabolic tip is usually exploited. The tip shape in the Sneddon’s model is described with equation $z=cx^2$, where $c$ is a parabolic focus. This equation is very similar to the Hertzian equation but does not contain maximum indentation depth limitation.

1.3 Mechanical models for multilayered systems

There are several methods for the evaluation of the elastic modulus of thin films on solid substrates, which include microindentation and bending experiments. As suggested in these approaches, the compression of the layered elastic solids (e.g., a compliant film on a stiff substrate) results in concurrent deformations of two or more interfaces with local deformation depending upon the mechanical properties of layers and a load transfer between adjacent layers (Figure 2).

Figure 2: Simultaneous deformation of several elastic layers for the layered solid by the AFM tip and corresponding parameters of the tri-layered model as discussed in the text.
Several different approaches have been recently developed to describe this phenomenon as will be discussed below.

A double-layer model was proposed to describe deformational behavior within a modified Hertzian approximation. The relation between a "modified" contact radius and Hertzian contact radius was suggested in the form:

\[
\frac{a}{a_{\text{hertz}}} = \left[ \frac{J^3 + 0.8 t}{1 + (0.8 t/a_{\text{hertz}})^2} \right]^{1/4}
\]  

(4)

where \(a_{\text{hertz}}\) is the contact radius calculated from the Hertzian theory and \(J\) is the ratio of elastic moduli of two layers. Limitations of this theory included the consideration of only a compliant layer on a stiff surface and the absence of the criteria for the selection of any interlayer interaction. Our previous use of this approach demonstrated that some improvement of the fitting procedure can be obtained for polymer films on solid substrates. However, for very thin films, this model usually overestimates indentation depth.

A more sophisticated model, which considered the elastic deformation of the layered solids with a certain transfer of the mechanical load between adjacent layers was proposed for the analysis of the microindentation data and was refined by several independent researchers. A general key point of this approach was the suggestion to represent the composite compliance of two-layered solids (e.g., a film-substrate system) as a superposition of individual compliances in the form:

\[
\frac{1}{E'} = \frac{1}{E_f} \left( 1 - e^{-\alpha h/t} \right) + \frac{1}{E_s} \left( e^{-\alpha h/t} \right)
\]  

(5)

where \(E_f, E_s\) are elastic moduli of the film and the substrate, \(t\) is the total thickness of the film, \(h\) is the indentation depth, and \(\alpha\) is a parameter defining contributions of different layers.
This representation is reminiscent of equation (3) for the composite modulus of two deformed solids in the mechanical contact. However, this approach introduces a new measure of a level of the transfer of the mechanical deformation between layers represented by a specially selected function, the transfer function, $e^{-\alpha h/t}$. This transfer function depends upon total thickness of the layer, indentation depth, and the properties of the inter-layer interactions as reflected by the parameter $\alpha$. The transfer function for the elastic layered solid has an initial small value for small, initial deformations ($h << t$) and increases for larger deformations ($h \leq t$).

The parameter $\alpha$ was initially suggested as an empirically determined parameter to be selected for each specific layered system. However, a clear physical meaning of this parameter was missing from the description proposed. Specific values of this parameter were experimentally determined and discussed for different pairs of solids but clear interpretation and understanding of differences observed not suggested. Some modifications of this transfer function for different layered systems were suggested to improve experimental data fitting. Another approach starts from the representation of the non-uniform depth profile in an analytical form as a function of indentation depth $h$:  

$$E' = E'_s + (E'_f - E'_s)\Phi(h)$$  

(6)

where $\Phi(h)$ is the transition function describing a specific shape (gradient) of the depth profile of the elastic modulus. In the framework of this approach, an indenter displacement and stress propagation in a layered medium were analyzed by using the modified Sneddon solution for homogeneous solids. Careful contact mechanics analysis led to a complex expression for the transition function in the form:

$$\Phi = \frac{2}{\pi} \arctan \frac{t}{h} + \frac{1}{2\pi(1-\nu)} \left[ (1-2\nu) \frac{t}{h} \ln(1 + (h/t)^2) - \frac{h/t}{1 + (h/t)^2} \right]$$  

(7)
Considering that such a complex function is cumbersome in routine data analysis, alternative simpler models were suggested and used for the analysis of experimental data. For instance, a simple linear transition function was proposed:

\[ \Phi = E_f - (E_s - E_f)h \]  

along with a more complex but still solvable exponential form:

\[ \Phi = e^{-\beta h} \]  

These approaches provided a good analysis tool for a variety of specific cases of the layered solids as has been recently discussed in detail. The comprehensive analysis conducted in this study demonstrated a reasonably good agreement of different approaches with the best fits obtained by using equation (7) and suggested some practical routines in implementing both experimental procedures and data treatment.

However, the models described can not be applied to some important systems or are indented for different experimental setups. Almost all mentioned above experiments were done by using microindenter that differs from convenient AFM technique. Different experimental routines should be developed and applied during indentation measurements with AFM. Another aspect, that limits applicability of mentioned above models, is that they were developed and applied for metal and other stiff systems. Only a few cases could be used to describe interaction between an indenter and polymer films because polymers have much smaller elastic moduli. And in case of thin polymer films, indentation occurs on a nanoscale level that is comparable with a size of several molecules.

Below, it will be shown that a generalized approach that starts with a definition of the depth profile as a smooth function with gradual localized changes provides a means for the
“visualization” of the transfer function for polymer layers and its concise interpretation for two- and tri-layer architectures.

1.4 Problem statement

As it was mentioned above, developed models have serious limitations. The most significant is that they are applicable primarily for two-layered systems when a more compliant layer is on top of a hard surface. Another set of limitations arises from the fact that most of them were developed for microindenter devices (with microscale contact areas) which cannot be applied directly to nanoscale experiments from AFM. The final limitation is that the experimental confirmations for the above mentioned models were obtained for relatively hard surfaces, such as ceramics and metals.

Additional set of problems is related to the AFM experimental setup. To receive reliable results it is necessary to develop a procedure that can confirm that the process was completely reversible, deformation was purely elastic, and morphology was not changed. Also, FDCs from experiments have inherent noise affects that can produce additional artifacts during data processing. This is why it is necessary to do some statistical smoothing before data processing.

The last problem is that there are only a few software developments that are capable of data processing directly from original microscope data files. Because AFM data files are complicated and large (512 lines of data in a non-organized ASCII file), it is nearly impossible to work with data from microscope software in data processing software and produce meaningful results. This is why developing a program block that is able to take experimental data directly from the AFM files is extremely important. In turn, direct data access requires additional software blocks that are responsible for smoothing and preprocessing analysis.
1.5 Goal

The ultimate goal of this research is to design a model that will be able to describe and quantify nanomechanical indentation of compliant surfaces based on the interaction of an AFM tip with a multilayered solid. The model should avoid the limitations discussed for the previous approaches and be able to analyze the surface behavior independently on the distribution of elastic moduli. The second step will be the selection and AFM testing of different multilayered solids under different conditions. The last step will be the writing of a multifunctional software tool that will be able to work directly with AFM files, to do necessary preprocessing steps such as curve smoothing, and to apply the model to data directly from multilayered experiments.

1.6 Objectives

1) Development and software implementation of a nanomechanical model for multilayered systems:
   a) Model development
   b) Software implementation
   c) Modeling on known systems with known parameters

2) Development and program implementation of tools for pre-processing experimental data:
   a) Force - distance curve smoothing
   b) Output data smoothing
   c) Viscoelastic analysis

3) Development experimental routines for collecting data for non-uniform polymer systems under different conditions:
   a) Controlling the sensitivity of the piezo element
   b) Completely reversible deformation
   c) Stable scanning

4) Set of experiments for selected multilayered systems:
a) Single molecule experiments  
b) Polymer brushes under different conditions  

5) Adaptation of the new model for the analysis of the AFM experimental data

1.7 Approaches

The approaches used can essentially be split into three categories. The first approach includes the design of multilayered films for experimental investigations. Two incompatible polymers, one a typical glassy polymer and another one a rubbery polymer, are randomly grafted onto a silicon wafer via the grafting-from method producing thick (20-150 nm) dense mixed brush layers. The resulting layers possess a nanostructured surface exhibiting either complete vertical or a combination of vertical and lateral microphase segregation of the two components. Since the glassy and rubbery polymers are mechanically dissimilar at room temperature, FV experiments should be able to show two clear levels of elastic response.

The second approach is focused on the evaluation of the interaction between the AFM tip and different surfaces. For instance, in the case of single molecule probing, FV experiments will allow for visualization of nanobjects, but experimental setup must be designed to eliminate tip/sample adhesion. To reduce strong attractive forces, tip modification should be conducted.¹⁷

The third part is related to the software development. When FV experiments are completed, a 3D file with all the FDC data is stored. The FDCs will be extracted from the file and converted into indentation-load curves. The indentation-load curves can be used to calculate the distribution of elastic modulus with depth. The recalculated loading curves will be transferred to the program block with the model. From here, nanomechanical parameters (for instance, elastic moduli, layer depth, and interfacial zones) can be obtained.
CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 Atomic Force Microscopy

As mentioned above, the main instrument for nanomechanical testing used in this work is the AFM. The advantage of this technique is that it provides information about elastic properties of materials and data about morphology simultaneously, with nanoscale resolution, thus being truly unique in this regard. Experiments were done for samples from different sources. The standard experimental procedure was applied. Detailed below is a description of methods used for testing with a description of the physical processes occurring during scanning and FDC data collecting (Figure 3). Experiments for ultrathin, layered polymer surface coatings with different microstructures were conducted on Dimension 3000 and Multimode Nanoscope III AFM (Digital Instruments) (Figure 4). There are two main parts responsible for AFM scanning: the scanner (piezo element) and head. The samples are mounted on the scanner (or stage, as in the Dimension). There are two scanner designs: either the sample is mounted on the piezo (Multimode) that is moving, or a tip is mounted on the piezo (Dimension). The head of the Multimode consists of a tip on which a small laser beam is focused, a mirror for redirection of laser reflection from the tip, and a detector that receives a signal and sends it to the controller to adjust scanner movement.

Figure 3: Force-distance curve for AFM is divided into several segments: (a) approach; (b) jump to contact; (c) compression mode; (d) unloading mode; (f) tip pull-off; (e) moving away from the surface.47
Figure 4: Scheme of the DI Multimode AFM (left); head of the microscope showing laser trajectory (right top); schematic representation of beam reflection from the cantilever to detector (right bottom) (from manual for Multimode AFM).

One of the main features of AFM, which is heavily utilized for this project, is the capability to obtain FV images. This provides the possibility to measure elastic and adhesive properties of the sample. It also collects data about sample morphology, concurrently with these mechanical properties. As it was mentioned before, the data are stored as an array with FDCs.

FDCs consist of several parts (Figure 3): during segment (a) a tip is far from the surface and any tip-sample interactions are absent. At point (b) due to the attractive capillary force between the tip and the surface the tip jumps to contact. Segment (c) is responsible for the
loading process or indentation of the tip into the surface. This part is the most important for
the model: data from the tip deflection can be used for elastic modulus calculation as well as
distribution of the modulus with the depth. Segment (d) is tip withdrawal from the surface,
while at (f) the tip loses contact with the surface because adhesion forces became smaller and
during (e), we have similar case as (a), in which the tip moves far from the surface and tip
deflection is zero. Tip deflection during segment (c) can be measured and converted to a
Indentation Load curve because indentation (penetration) is equal to probe position minus tip
deflection (Figure 1).

2.2 Tip radius measurements

In order to quantify the experimental AFM data, we measured the tip radius or coefficient \( b \)
of parabola \( Z = b \times X^2 \), which approximates the tip shape. By imaging reference samples of
gold nanoparticles with dimensions from 5 to 30 nm, the tip end shape was approximated by
a parabolic function to deduce effective tip radii within 10–50 nm. The radius of the contact
area, estimated with the Hertzian model, was within 1–50 nm.

Figure 4. Parabolic model for the tip radius. (From the MMAnalysis manual by V. V.
Gorbunov)
2.3 Cantilever spring constant measurements

For spring constant calibration of the cantilever, as the main technique “Cantilever-against-Cantilever” technique is used. In this technique the cantilever with known spring constant is used as a reference cantilever (see Figure 5).

![Diagram of cantilever measurement](image)

Figure 5. Tip on tip experimental model (From the MMAnalysys manual by V. V. Gorbunov)

The force balance in the point A (see Fig. ) is:

\[ F_{\text{test}} = F \leftrightarrow k_{\text{test}}h_{\text{test}} = kh \]

The spring constant of the tested cantilever is expressed with equation:

\[ k = k_{\text{test}} \frac{h_{\text{test}}}{h} \]

where: \( h_{\text{test}} \) is deflection of the test cantilever, \( h_{\text{test}} = H - h \); \( H \) is the Zpos of the tested cantilever; \( h \) is the deflection of the tested cantilever.

Another method of spring constant calibration is based on resonance frequency methods when the relationships between the spring constant and the resonance frequency are calculated by finite elements method for different kinds of cantilevers.\(^{45}\)
2.4 Force Volume measurements

Experimental procedure were conducted in a dry environment and in fluid according to the experimental procedures described elsewhere.\textsuperscript{46,47} Silicon (and Si\textsubscript{3}N\textsubscript{4}) tips were selected for these tests. The range of spring constants varies from 0.5 to 50 N/m depending on the sample. Sensitivity of the piezoelement for the given cantilever is carefully measured on a bare silicon wafer right before and after probing. Tapping-mode (TM) images were obtained to identify surface areas and to confirm that deformation is completely elastic without sample damaging. FV micromapping with a number of pixels from 16 x 16 to 64 x 64 is conducted on several selected locations for selected areas from 200 x 200 nm to 2000 x 2000 nm. TM imaging is repeated after micromapping to ensure preservation of initial surface morphology. It was found that numerical values obtained from FV experiments are measured with the accuracy around 15 percents.

More complicated experimental setup is required for FV measurements in a fluid environment. The usual preparation procedure becomes more sophisticated because of the additional steps when an operator adds liquid. The operator adds a droplet of the fluid with necessary size (20 – 50 µL) to cover part of the sample but it should not exceed the level where the droplet interacts with surrounding materials. This can result in additional sample contamination and unstable scanning during the experiment. After the fluid is added, the operator should realign the position of the detector and the mirror. The aligning should be done only one time before sensitivity measurements. After that, the sample should be exchanged and the same kind of liquid should be used.

To conduct experiments when the liquid consists of several components or when one component is exchanged by another, it is necessary to select fluids that have either similar evaporation rates or similar reflectivity index to prevent the laser beam from misalignment on photodetector.
CHAPTER 3

SOFTWARE/MODEL DEVELOPMENT

3.1 Derivation of the model

The next model with a non-uniform function for elastic modulus was developed to avoid limitations that are presented in other approaches. Any variation of the elastic modulus along the vertical coordinate $h$ (indentation depth) can be represented as a constant level superimposed with a combination of positive and negative local deviations:

$$E'(h + \Delta h) = E'(h) + mE'(h)\Delta h - nE'(h)\Delta h$$

(10)

This equation represents a change in the current value of the elastic modulus in the $\Delta h$ range as the previous value, $E'(h)$, plus a combination of increasing $mE'(h)\Delta h$ a decreasing $nE'(h)\Delta h$ contributions, thus giving an expression for a local gradient as:

$$\frac{\Delta E'}{\Delta h} = (m - n)E'(h)$$

(11)

In differential form and with $k = m-n$ representing a continuous balance of local deviations of the elastic modulus, this equation can be represented as:

$$\frac{dE'}{dh} = kE'(h)$$

(12)

For a smooth monotonic function without singularities, it is natural to suggest that coefficient $k$ depends upon the overall difference between moduli of two layers because larger local changes are generally required to accommodate larger overall difference in
properties between adjacent layers. For the sake of simplicity, let's assume that coefficient $k$
linearly depends upon difference between a current modulus value and overall difference in
elastic moduli of adjacent layers and $\alpha$ is a proportionality coefficient:

$$ k = \alpha((E_i - E_o) - E'(h)) \quad (13) $$

where $E_o$ and $E_i$ are two levels of the elastic modulus for a two-layered system (Figure 4).
The proportionality coefficient $\alpha$ can be either positive or negative depending upon overall
gradient of the elastic properties (compliant on stiff or stiff on compliant).

With this assumption, equation (12) can be rewritten as:

$$ \frac{dE'}{dh} = (\alpha((E_i - E_o) - E'))E' \quad (14) $$

If a new variable is set, $M = E_i - E_o$, the equation (14) is transformed to:

$$ \frac{1}{M} \left( \frac{dE'}{E'} + \frac{dE'}{M-E'} \right) = \alpha dh, \quad \Rightarrow \quad \left( \frac{dE'}{E'} + \frac{dE'}{M-E'} \right) = \alpha M dh \quad (15) $$

After integration the next equation will be obtain:

$$ \ln(E') - \ln(M - E') = \alpha Mh + C \quad (16) $$

where $C$ is the integration constant defined by the initial conditions.

If the "reference" depth $h_o$ is defined as a point where the modulus equals half of the
difference between the two layers, $E'_o = M / 2$, then equation (16) is transformed to:

$$ C = \ln(E'_o) - \ln(M - E'_o) - \alpha M h_o \quad (17) $$
After substitution, a new equation will be obtained:

$$\ln \left( \frac{E'(M - E'_0)}{(M - E')E'_0} \right) = \alpha M (h - h_0) \quad (18)$$

that can be converted to the final form after proper substitutions:

$$E' = \frac{E'_1 - E'_0}{1 + \exp(-\alpha(E'_1 - E'_0)(h - h_0))} \quad (19)$$

A selection of a sign for $\alpha$ depends upon a gradient sign as was mentioned above. Let's introduce a new variable $\alpha' = \alpha E'_1 h_0$. In this case equation 19 can be rewritten as

$$E' = \frac{E'_1 - E'_0}{1 + \exp(-\alpha'(E'_1 - E'_0)(h - h_0))/(E'_1 h_0))} \quad (20)$$

Overall, the depth profile of the elastic modulus for a two-layered system can be described as a superposition of the initial level and variable contribution for the two-layered system (20) as:

$$E(h) = E_0 + E'(h) \quad (21)$$

Modulus profile in this form can be directly used in equation (2) for fitting experimental data for the elastic response at a variable indentation depth.

The description proposed here is based on simple initial assumptions on the gradient properties of the layered systems and very basic arguments. It combines all major features suggested separately in several approaches discussed above, and leads to a relatively simple equation (20) for the description of the elastic modulus gradient for two-layered systems. For the important case of a compliant film on a stiff substrate, only two unknown variables can
be varied to fit experimental data (the elastic modulus of the top layer and parameter \( \alpha' \)) assuming that the elastic properties of the substrate are known. The proposed approach allows for the analysis of different layered structures. General profile of two-layer elastic modulus distribution as described by equation (20) is presented in Figure 6. Two different levels of the elastic modulus are separated by a transition zone with a gradient of the elastic properties.

![Figure 6: The visualization of the depth profile for a hypothetical stiff-compliant film with two different levels of the elastic moduli (\( E_o = 160,000 \text{MPa} \) and \( E_1 = 30,000 \text{MPa} \)). The interfacial zone, \( T \), is defined for this profile as discussed in the text.](image)

3.2 Model properties

The variation of the elastic modulus in a wide range creates different profiles including a virtually uniform distribution for a layered system with a small difference in elastic moduli (Figure 7).
Figure 7. a) Influence of the transition parameter $\alpha$ on the overall shape of a hypothetical two-level depth profile of the selected elastic moduli. b) Influence of the elastic modulus of the topmost layer on the total depth distribution of the elastic modulus of the two-layered solid.
The width of this transition zone between two layers is determined by the parameter $\alpha$ through the transition function. A high value of this parameter corresponds to a very sharp interfacial zone resulting in a step-like shape of $E'(h)$ (Figure 7). Decreasing $\alpha$-value results in a gradual broadening of the step-function with the formation of a virtually continuous gradient for a very low value of $\alpha$ (Figure 7).

For practical purposes, instead of "non-transparent" parameters $\alpha$, we introduce the thickness of the transition zone as the major fitting parameter as illustrated in Figure 6. We calculate the "effective" thickness of the transition zone, $T$, as a distance between two points representing the intersections between two levels of elastic moduli and the slope to the fitting curve in the point where the value equals the average of the above mentioned moduli. This parameter has direct physical meaning as a measure of the sharpness of the transition zone between layers (see Figure 6 for the definition of the thickness of the transition zone). A reasonable physical value of this parameter and its correlation with expected or known structural gradients (e.g., controlled by processing, deposition, or synthetic routine) are important verifications of the concept and the fitting procedure as will be discussed below.

The advantages of the approach proposed is that it can be extended to more complicated cases of tri- (and more) layers by modifying equation (18) to include a recursive extension toward complex graded functions. For example, for the tri-layer structure, the model includes two independent values of the elastic modulus and the transition zone as fitting parameters assuming that the substrate properties are fixed (see Figure 8).
Figure 8. a) The variation of the transition parameter $\alpha$ in a hypothetical tri-layered system with selected values of elastic moduli. Decreasing $\alpha$ results in the broadening of the transition zone and disappearance of the sharp steps. b) Influence of the elastic modulus of the interlayer on the depth distribution of the elastic modulus of the tri-layer system presented above.
The corresponding complex but still analytically solvable expression can be derived from (18) as follows:

\[
E' = E_0 + \frac{E_2 - E_1}{1+ \exp(\alpha_1(E_2 - E_1)(h - h_0))} - E_0 \frac{E_2 - E_1}{1+ \exp(\alpha_1(E_2 - E_1)(h - h_0))} - E_0 (h - h_0) \]

with \( E_0, E_1 \) and \( E_2 \) representing three levels of the elastic modulus for the tri-layered system (Figure 8).

Using this expression, a tri-step graded function can be simulated to analyze the surface structure with a complex profile of stiff-on-compliant-on-stiff type (Figure 8). By the variation of the transition zone gradient, this step-function can be converted from a sharp step function to a smooth function with a minor depletion in the middle (Figure 8). On the other hand, by changing the level of the elastic modulus for the intermediate layer, this function can be converted to the tri-layer function with ascending or descending elasticity (Figures 8-9). Increasing of the thickness of the transition zone results in gradual transformation of the graded function to a smooth continuous gradient with virtually any shape (Figure 9). And, unlike analytical functions with poorly defined boundary conditions used previously for the representation of the transition function, \( \Phi(h) \), these graded functions contain clearly defined and separated physical parameters for controlling the level of the elastic modulus and gradient properties.

It is worth noting that in Figures 6-10, the absolute values of the elastic modulus and the indentation depth were selected only for illustrative purposes, can be very different for different layered models, and are not to be used for the comparison between different layered models.
Figure 9. Variable profiles of a hypothetical multilayered system with compliant-stiff-more stiff and stiff-compliant-more compliant layers and different transition parameters \( \alpha \): sharp steps, steps with interfacial zone, and continuous gradient \((E_o < E_i < E_2 \text{ and } E_o > E_i > E_2)\).
In the same way, it is possible to build even more complex layered systems such as the four-layer profile presented in Figure 10. To show the depth behavior of the elastic response in this system, a set of the tri-layer film with decreasing elastic modulus located on a stiffer substrate was selected. The theoretical loading curve showed a non-monotonous behavior, which adequately reflected the complex elastic response of this system (Figure 10). As it was mentioned above in all these examples, both depth and elastic modulus values were selected for illustrative purposes only to reflect relative variations without any intention to compare absolute values for different profiles.

![Figure 10. A hypothetical model of a four-layered coating in the case of stiff-compliant-more compliant-more stiff layering. a) the depth distribution of the elastic modulus with smooth transition zones. b) corresponding loading curve expected for this distribution.](image)

Here, it is important to mention several other critical contributions, which could affect force-distance data and are not accounted for in the model discussed here. First, strong adhesion between the AFM tip and surface can disturb the initial portion of loading curves and result in significant overestimation of the elastic modulus level at small indentation depth. This contribution was analyzed in other publication and demonstrated significance of the adhesion hysteresis and initial non-zero contact area for very compliant polymeric materials with high adhesion (e.g., polar rubbery layers with the elastic modulus below 2 MPa and surface energy much higher than 20 mJ/m²) in air. For these materials, an application of the Hertzian model resulted in manifold overestimation of the elastic modulus for small indentations. A complete Johnson-Roberts-Kendall model should be applied that
makes consideration significantly more complex and requires additional non-trivial measurements. However, for compliant materials with modest adhesion and higher stiffness, this overestimation is limited to a few initial several data points and, thus, the approach discussed here can be applied. Second, a viscous contribution (time-dependent mechanical properties) can be critical in defining an overall shape of loading curves for viscoelastic polymeric materials. As it was discussed earlier, this phenomenon would result in a concave shape of the FDCs, which, in fact, is sometimes observed\textsuperscript{47,35} This contribution can be treated by applying Johnson's recent development\textsuperscript{49} as was discussed in some publications.\textsuperscript{50,35} For the analysis discussed here, we selected materials without significant viscous contributions (far from the glass transition temperature where a contribution of the loss modulus does not exceed 10-20\% of the elastic modulus value\textsuperscript{51} ) and probing frequencies in the range of minimal time-dependencies as was discussed earlier.\textsuperscript{52} Third, the surface roughness of the layers studied here is extremely low, thus, virtually eliminating any significant scattering in the first few data points observed for rough surfaces.\textsuperscript{44} In fact, the surface microroughness does not exceed 0.2-0.5 nm for some layers studied here. Forth, wrong selection of contact point can result in incorrect data interpretation. As a result zero indentation point can be significantly shifted from the real position and distribution of elastic moduli will be disturbed. That's why before elastic moduli calculation the FDCs averaging is done to clarify the point of contact.

Finally, in all instances discussed here, we used a loading portion of the experimental force-distance data for modulus estimation. This is justified by the fact that for purely elastic deformation, loading and unloading portions should be identical, which was indeed demonstrated for a number of compliant polymer surfaces.\textsuperscript{52} The use of the unloading portion of FDCs is more complicated because some data points are affected by adhesive properties and the pull-off point cannot be easily defined. Below we will show one example of unloading portions of the experimental data. In addition, in our evaluation of the elastic modulus for the topmost layer, as initial parameter for the input in fitting procedure, we used apparent value of the elastic modulus extrapolated to zero indentation depth. In many cases, the final value for the best fit was fairly close to this value.
As it was discussed, the model obtained doesn’t have limitations that exist in other mentioned above approaches. Using relationship (20) it is possible to obtain fitting parameters for one set of experimental data with known parameters (see Figure 11).

Figure 11: Left top: Sketch of the sandwich coating with stiff-compliant-stiff sequence of layers fabricated from grafted polymer layers of different types (stiff topmost layer, rubbery interlayer, organic SAM, silicon substrate).  Right top: Experimental individual FDCs (loading runs, curves are offset for clarity) and the average loading run for this tri-layer film. Right bottom: The depth distribution of the elastic modulus for the tri-layered polymer system and fitting with the tri-layer model (solid line). Left bottom: Fitting of the experimental loading curve (circles) by the tri-layered model (solid black line, almost completely screened by experimental data points) and the best fit with Hertzian curve (dot line).
This polymer “sandwich” system was prepared by grafting the rubber polymer interlayer of 10 nm thickness to functionalized self-assembled monolayer on a silicon wafer and capping this interlayer with a photopolymerized stiff polymer topmost layer with the thickness between 10-30 nm. This model represents a complex tri-layer system with elastic modulus changing from 2,000 MPa for the topmost layer to 5-10 MPa for the rubbery interlayer on 160,000 MPa silicon substrate as was independently measured for these materials. In fact, the FDCs collected on different surface locations demonstrated clearly a non-monotonic character with three different local slopes as is better visible of the average curve. This non-monotonic character became more visible on the loading curve, which showed pronounced S-shaped behavior and it is different from DC (Figure 11). Attempts to fit the experimental data with Hertzian model failed: significant deviations were observed in the range of either low or high deformations depending upon the selection of the elastic modulus value (Figure 11).

However, the experimental data could be fitted with a tri-layer model with modest gradient in the transition zones as demonstrated in Figure 11. The best fit has been achieved with the tri-layer model composed of the topmost stiff layer of 5 nm thick with the elastic modulus of 2,000 MPa, a central interlayer of 20 nm thick and the apparent elastic modulus of 800 MPa, and the solid substrate with the elastic modulus of 160,000 MPa (Figure 11). The ultimate indentation of the tri-layer film was about 35 nm, which was close to the total thickness of the tri-layer film and indicated virtually complete compression under very high mechanical load. The thickness of the transition zone does not exceed 10 nm that indicates modest gradient distribution between layers within the layered coatings.

### 3.3 Pre-existed software block

The model developed was built in already existed software developed by V. V. Gorbunov. This software was created to process the data files from Nanoscope III AFM software that contain data either as a FV set of FD curves or as a single FDC. Also the
software contains several blocks that contain necessary data processing tools to provide calibration measurements for tip radius and cantilever spring constant.

The pre-existed software block operated in several step.

1) During the first step data from original was read and conclusion was made if the file contains FV data or a single FDC.

![Initial data](Image1)

![Resulted data](Image2)

**Figure 12.** Data transfer between AFM software and MMAnalysis. Two standard kinds of AFM files are recognized by the software and are opened as either FV picture (left) or FDC picture (right).

2) The second step includes the model selection and appropriate calibration parameters input. Figure 13 contains all necessary initial parameters to have successful data processing. The
most important parameters are marked by numbers: 1) Tip radius, cantilever spring constant and Poisson’s ratio that are determined from independent measurements; 2) Sensitivity value. The box shows initial value and operator is able to put new one. It was important step in software development because very often measurements are failed because of changing sensitivity during the experiment and ability to change this value later allows an operator to observe possible properties of the sample and accordingly be able to change scan settings before the next experiment; 3) Selection of initial point (point of contact) on FDC curve. An operator can either select point of jump in contact or point where deflection was zero as initial point for elastic modulus evaluation; 4) Selection of analysis mode when either changing of curve or changing of the curve slope is considered for analysis; 5) Model selection. An operator can select either Hertz/Sneddon model or JKR model; 6) A button for beginning of calculation.

Figure 13. Software windows that contain initial parameters. See the text for every parameter description.
3) Output data include FDCs for selected point (in case of FV), Penetration (Indentation) 
Load curve and ability to apply different methods for elastic moduli estimation from the data 
obtained.

Figure 14. Standard output window. Several important blocks are pointed by the 
arrows that includes windows with FDC and Indentation Load curve.

3.4 Software implementation of the model

3.4.1 Data transfer between blocks

The software described above was adapted for the multilayer analysis. In case when two or 
more layers are present the information can be transferred to the separate block that contains 
tools for described above model. Multilayer Block (MB) receives from the main part of the 
software the information about FDC as two dimensional array.
Data is transferred as a two dimensional array that contains FDC. After that the operator has ability to input necessary calibration information and select the range of data analyzing.

3.4.2 Panels and Controls

The main panel contains several tools that are necessary for data fitting. Below there is a description of every tool.
1) A window with initial calibration data about the experiment such as tip radius, cantilever spring constant, Poisson’s ratio

2) A window with resulting fitting data. Data output contains information about elastic moduli of all layers, values of transition parameters and values related to the width of interfacial zone

3) Number of fitting intervals. Increasing the number results in increasing of the accuracy but at the same time the calculation speed goes down

4) A button that is responsible for adding number of fitting layers. By default only substrate is present in the window. An operator can add as many as he wants layers to the model

5) A button for removing excessive layers

6) A button that is responsible for redrawing fitting curve. After each changes (selection/adding/removing layers, manual changing of fitting parameters) the button should be pressed

7) Options for switching between different fitting windows. An operator can fit either Indentation Load curve or distribution of elastic moduli with indentation (Figure 17).

Figure 17. Windows with fitting curves. The left window contains FDC, the middle has Indentation Load and fitting curves and the depth distribution of elastic moduli is represented in the right window.

8) Ability to put the initial/fitting data into the file/clipboard
3.4.3 Data processing

The data processing block is designed in a way that the software, using the user defined fitting parameters, builds the theoretical curve according to the equation (20). To start the fitting procedure, the operator should recalculate the Indentation Load curve using appropriate parameters. After that, the number of model layers should be determined. Usually it is possible to evaluate the number of layers based on the number of regions on the Indentation Load curve that have different slopes. In the example above, it is possible to see that the curve can be divided into two regions: the first is almost vertical and the second is horizontal. It is additional requirement of the model that parameters about the substrate should be known. By default, the software automatically inputs parameters for the typical substrate – silicon – and the operator should change the value if another material is used. After applying changes, some initial theoretical curve will appear that corresponds to the initial input parameters.

Figure 18. After inputting some initial or default values some initial fitting curve appears.
The next step is selecting the first approach for elastic modulus and $h_0$ value. For the $h_0$, it is possible to put the value where the slope of Indentation Load curve changes dramatically.

![Graph showing indentation load and depth profile with data points and curves indicating the change in slope.](image)

Figure 19. A more correct fit when an operator selected more appropriate parameters. During this step, the shape of theoretical curve should be similar to experimental.

The fitting procedure includes changing of three main parameters: Depth parameter ($h_0$), $\alpha$, and elastic modulus for the layer. Usually, $h_0$ and $\alpha$ influence the shape of the curve while the elastic modulus only affects the overall slope. It is recommended to fit the shape of the curve first and the whole curve later.

![Graph showing indentation load and depth profile with data points and curves indicating the change in slope.](image)

Figure 20. Final fit when the theoretical curve is in the closest position to the experimental data.
To reach the perfect fit the operator should have good theoretical curves in all windows at the same time.

![Graph showing theoretical curves and depth profiles](image)

**Figure 21.** Theoretical curve in the Depth profile window is rebuilt together with the Indentation Load curve. In case of the perfect fit both FDC and depth profile should be repeated by the theoretical curve.

### 3.4.4 Results output

Every data window with fitting curves could be saved either to clipboard or to ASCII file that can be used later in Origin or Excel software. ASCII file contains two two-dimensional arrays with original experimental data and theoretical curve. The fitting parameters window contains all obtained results (Figure 22).

<table>
<thead>
<tr>
<th></th>
<th>Young</th>
<th>Poisson</th>
<th>Depth x Par.</th>
<th>ratio 'a' x10000</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate</td>
<td>180000</td>
<td>0.3</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>layer 1</td>
<td>285.6</td>
<td>0.3</td>
<td>0.6523972</td>
<td>1.13848</td>
</tr>
</tbody>
</table>

**Figure 22.** Window with fitting parameters
3.5 Other software implementations

3.5.1 Viscoelastic model

As it was mentioned before, viscoelastic factor plays very important role for data analysis. To receive reliable elastic modulus data it is necessary to minimize effect of viscoelastic component. To do this operator should work far from $T_g$ temperature. In case when the contribution is present and visible the software block was added.

To analyze the loading rate dependence behavior of a surface layer Maxwell or Voigt-Kelvin models are used, as well as Johnson’s suggestions for the contact area, loading rate, and other contact parameters. Comparing theoretical results with experimental curves the estimation of the viscous-elastic parameters of the sample can be made.

Johnson model

Three-parameter equation can be used to calculate the indentation depth as a function of the loading time:

$$h^2(t) = h^2_{\text{Hertz}} \left[ 1 - \frac{1 - k}{\tau} (1 - e^{-\tau}) \right]$$

where the $h^2_{\text{Hertz}} = \left[ \frac{3P}{4E_\infty \sqrt{R}} \right]$ is the indentation depth from the Hertz theory; $\tau = \frac{t}{T}$ is the ratio of the relaxation time of a material and the time when the load is changed from 0 to $P$; the $k = \frac{E_\infty}{E_o}$ is the ratio with $E_\infty$ and $E_o$, which are the static and the momentary Young’s modules correspondingly.
Voight-Kelvin model

This is two-parameter model takes into consideration only the static Young’s modules $E_\infty$ and the relaxation time $T$:

$$h^2(t) = h^2_{\text{Hertz}} \left[ 1 - e^{-\tau} \right]$$

Maxwell model

This is the two-parameter model can be used for materials with the relaxation time much longer than the time of loading $\tau \ll 1$:

$$h^2(t) = h^2_{\text{Hertz}} \left[ 1 + \tau \right]$$

Figure 23. Theoretical calculation of the loading curves for a polymer surface with a variable relaxation time from Johnson equation. The curve shape becomes concave while relaxation time increases.
3.5.2 Input and output data smoothing

An important development was done that is related to data smoothing. Due to the different reasons experimental FDCs have different deviations that can be result of noise or other influences. These deviations are smaller than the sensitivity of microscope but they can produce artifacts that can confuse an operator during analysis. The block was added to the software that is able to do averaging for the set of curves. Figure 24 represents how a set of FDCs can be averaged into a smoothed curve.

![Graph showing smoothing of FDCs into one average curve](image)

**Figure 24.** Smoothing of FDCs into one average curve. It is possible to observe that the average curve is free from small deviations that are below the sensitivity of AFM.
To do an averaging, an operator just activates the window with averaging, and after that collects statistics on the main window. In case that the operator does not like the curve, it can be unchecked and the curve will not be accounted for during the smoothing (Figure 25).

Figure 25. FDC window with “Averaging” sub-window. An operator can activate/deactivate an entire set or single curves.

An additional improvement for data smoothing was developed for the output data. Depth distribution of elastic moduli was previously calculated according to the following algorithm: the Indentation Load curve was divided into N subcurves and modulus data was obtained separately for each subcurve. Due to the presence of noise and other small deviations, the resulting data were presented in a way that an operator may not have a clear understanding about the general tendencies (Figure 26).
Figure 26. Elastic moduli distribution. An operator is able to select the number of intervals in which the original Indentation Load curve will be divided to receive the depth profile.

Due to this reason, the next approach was developed. The operator can select the number of points N on the Indentation Load curve and the elastic modulus is recalculated for each interval (every next interval covers N-1 points from the previous) on the Indentation Load curve. It is possible to see (Figure 27b) that after smoothing on 15 points the general behavior becomes more visible: elastic modulus first goes down around 150 nm and after that, it goes up because of the substrate presence; that corresponds to the typical tri-layered system and can be used for selection of number of layers for multilayered analysis. An
intermediate stage is shown for smoothing at 5 points in Figure 27a. For 5 points, the smoothed picture is still unclear. However, the general tendency becomes visible although not enough yet to make conclusions about number of layers.

Figure 27a. The previous data smoothed on every 5 points. It is enough to see the tendency, and it is possible to say that the elastic modulus start to grow under deep indentations but it is possible to determine number of layers.
Figure 27b. The previous data smoothed on every 15 points. Tri-layered system becomes more visible.
Chapter 4
Different Multilayered Systems

4.1 Single molecules and aggregates on a substrate

An understanding of nanomechanical properties of individual organic and polymeric molecules and their molecular aggregates is critical for the design of the nanoscale contact interactions in nanodevices of electromechanical and fluidic types. Current approaches are limited by qualitative visualization of the surface distribution with AFM. A lateral resolution usually is appropriate for the observation of individual molecules or their aggregates even considering significant tip dilation. Alternatively, within a force spectroscopy approach, FDCs are collected for multiple, unspecified surface locations and pull-off forces are used for the evaluation of specific interactions or the tensile properties of molecules. Direct correlation between the surface nanostructure and the nanomechanical properties could not be readily obtained within this approach. A main disadvantage of this method is that an object studied, as a rule, should be long (usually hundreds of nanometers). Many experiments, thus, are focused on DNA, proteins, and high molecular weight functionalized macromolecules. Another problem of this method is that, without concurrent topographical measurements, it’s virtually impossible to determine what was, in fact, being stretched: molecules, bundles of molecules, substrate, or something else.

An alternative approach includes the micromapping of selected surface areas via a collection of FV data composed of an array of FDCs and the analysis of the indentation-deflection behavior with the AFM tip engaged in compression mode. Under optimal probing conditions, an application of the contact mechanics model to this compression mode (either Hertzian or Sneddon) could produce a reliable value of the elastic modulus, surface distribution of surface stiffness of elasticity, and even the depth profile of the elastic modulus. This approach is applicable to molecularly thick compliant films, nanoscale colloidal particles, and nanoparticulate molecules and can provide reliable information with lateral resolution below 10 nm and vertical resolution below 0.2 nm.
The set of measurements were done for the elastic properties (stiffness or elastic modulus) of individual nanoparticulate molecules with an effective diameter below 3 nm and their surface aggregates containing a limited number of molecules (several dozens). Dendritic molecules, namely, hyperbranched polyesters (Figure 28), were selected which are known for forming compliant nanoparticulates with a diameter of several nanometers. Internal architecture of these molecules could be represented as a highly branched, tree-like structure with a central core, branches, a certain level of internal cyclization, and high concentration of terminal functional groups. These molecules represent a new class of functionalized materials with promising interfacial nanoscale properties as discussed in recent publications.

Figure 28. Chemical structure of dendritic molecules (top) and corresponding molecular models (bottom) for G3 (a) and G4 (b)
4.2 Single molecules sample preparation

Materials. We study third (G3) and four (G4)-generation dendritic molecules, hyperbranched polyesters (molecular weight of about 3000 to 7000, respectively). Commercially available hydroxyl-terminated hyperbranched polyesters were donated by Perstorp Polyol Inc. These molecules possess slightly flattened and spherical conformations on solid substrates with dimensions of about 2.5 and 3 nm for G3 and G4 molecules, respectively. Corresponding bulk materials are tough polymers with a relatively high glass transition temperature (82°C for G4 and 72°C for G3 as was determined from DSC measurements on a Pyris 1 instrument).

Sample preparation. The substrates were atomically smooth silicon wafers of the {100} orientation with one side polished (Semiconductor Processing, Co.) and modified silicon wafers with NH₂ SAM. Silicon wafers were treated in an ultrasonic bath for 10 minutes followed by a “piranha” solution (30% concentrated hydrogen peroxide, 70% concentrated sulfuric acid) bath for one hour. After “piranha” bath, the samples were rinsed several times with Nanopure water (18 MΩ cm) and dried under a stream of dry nitrogen. Deposition of hyperbranched molecules onto the substrates were carried out by adsorption from acetone solution according to the procedure described earlier. Silicon substrates with size of 20x20 mm were put into 0.5 g/L concentration solution at room temperature for 3 hours.

4.3 Polymeric brushes

4.3.1 Structure and definitions

In this research the main attention is related to binary brushes because of their specific properties and set of advantages comparing with single brushes. The brush system should have two components with completely different properties that can be mechanical, chemical. To have an optimal system for testing one component should be in a glassy state and another in a rubbery state. There are two ways how to create a binary system. The first one includes
the case when both components are grafted independently. In this case it is possible to vary grafting density. Another case is when both components are part of one molecular. In this case every grafted molecular has two arms with completely different properties. Each component can be swollen or collapsed according to the external conditions (pH, light, surface pressure etc.), solvent, and temperature. From different sets of combinations as well as polymer choices it is possible to create huge amount of different materials that can possess unique morphologies, physical properties, responses to external environments. All of this gives to polymer brushes much more wide set of properties than can be present in one component brushes and SAMs. The two component brushes can be used as coating for a “smart” material, which has ability to respond to external stimulation. To summarize, in polymer surface science, it is desirable to create densely grafted polymer brush layers that possess superior wear resistance, elastic deformation, and morphological properties over those of conventional SAMs. This is a result of the recent advancements in nanotechnology. The concept of polymer surfaces functioning merely for lubrication enhancement is no longer the aim. Now, in addition to acting as lubricating films, polymer surfaces must be able to respond to the environment and have adaptive properties so they can be tuned for certain conditions such as wettability and adhesion. The challenge for the polymer surface engineer is to build all these desirable functionalities into one single layer. As was mentioned in current work two kinds of brushes were investigated the first one is two components brush poly(styrene-co-2,3,4,5,6-pentafluorostyrene)/polymethylacrylate (PSF/PMA), where both components were grafted independently.

Figure 29. Initial materials for creating two components brush (PSF/PMA).
And the second type is Y-shaped polymer brushes, polystyrene/polyacrylic acid (PS/PAA), when two different components are connected to the same leg (Figure 30).

Figure 30. Y-shaped brush with PS and PAA arms.\textsuperscript{91}

These brushes were selected for experiments because one component contains PS-elements that are glassy and another component is PMA/PAA that is in a rubbery state under usual conditions. As it will be shown below these two systems with completely different components are good examples for nanomechanical tests when it is necessary to show two regions with different elastic properties.

4.3.2 Polymer brushes in different environments

In this work, the concepts expressed above are taken a step further as two different polymers are grafted to the same surface, and each species reacts very differently with the
surroundings (Figure 31). Therefore, in the case of two-component or binary polymer brush layers, the variety of surface morphologies possible greatly increases depending upon the chemical composition. Surface composition and hence properties such as surface energy, adhesion, friction, and wettability have the possibility of being "tuned" to the necessary state. The recent development of binary brushes with proven reversibility between morphological states has allowed for much more diverse applications. 68

![Figure 31. Model demonstrating how a wide range of surface composition is possible in a binary polymer brush system. The top two schemes show selective environments for each polymer, bringing the favored one to the surface while the other collapses to avoid interaction. At bottom, the both chains favor the surrounding environment, and attempt to increase interaction with it by swelling. 92](image-url)

The polymer brushes have several practical applications, as well as several potential future applications that can have a significant impact on our lives. Again, it should be stressed that these mechanisms can be effective only if the polymer chains are strongly tethered to the substrate, and the surfaces are "smart". Brush layers are desirable because their surface properties and functionality can be easily altered, and the above applications require very
specifically tuned surface properties including tailored adhesion, lubrication, wetting, functionality, and adsorption behavior. In addition, brushes have the ability to be patterned and the chemical/physical nature of the surface can be highly controlled through switching, which makes brushes even more advantageous to conventional SAM coatings.

4.4 Brush sample preparation

Materials. Monomers. Styrene (S, Aldrich), 2,3,4,5,6-pentafluorostyrene (FS, Fluka), and methyl acrylate (MA, Aldrich) were purified with an aluminum oxide type 507C, neutral, 100-125 mesh (Fluka) chromatographic column. Solvents of analytical grade toluene, tetrahydrofuran (THF), and hexane were distilled after drying with sodium. Dichloromethane was dried over molecular sieves overnight, and methanol and ethanol were used as received. Initiators. 4,4'-Azobis(4-cyanopentanoic acid) (ABCPA, Aldrich) and 4,4'-azobis(isobutyronitrile) (AIBN, Fluka) were purified by recrystallization from methanol. All reagents were used immediately after purification. Water was cleaned with a Milli-Q ultrapure purification system, Ω >18.0 Mohm cm. Silicon wafers (Wacker-Chemitronics GmbH, Burghausen, Germany) were cleaned with dichloromethane and then in an ultrasonic bath mixture of NH₃ (25%), H₂O₂ (30%), and water in the ratio 1:1:10 at 60 °C and were rinsed several times with water. 3-Glycidoxypropyltrimethoxysilane (GPS, Aldrich), ethylenediamine (ACROS Organics), and phosphorus pentachloride (Merck) were used as received. Triethylamine (RiedeldeHaen) was dried on calcium hydride.

Introduction of Azo-Initiator. Silicon wafers were treated under an Ar atmosphere by 1% GPS in dry toluene for 16 h and afterward washed two times with dry toluene under Ar and three times with ethanol in an ultrasonic bath. In the second step, the Si wafers were treated with 2% ethylenediamine in ethanol for 1 h and washed three times with ethanol. Separately, a chloroanhydride derivative of ABCPA (Cl- ABCPA) was prepared. A suspension of 5 g of ABCPA in 50 mL of CHCl₃ and a slurry of 40 g of PCl₅ in 100 mL of CHCl₃ were mixed at 0 °C under an Ar atmosphere. The mixture was stirred overnight under an Ar atmosphere while it warmed to room temperature. CH₂Cl₂ was evaporated out under reduced pressure to
precipitate the major part of the dissolved PC15. The yellow solid of PC15 was filtered off. Cl-ABCPA was precipitated at 0 °C as a white powder in 300 mL of dry cold hexane, filtered and washed with dry cold hexane, and dried in a vacuum, giving 84% yield. In the next step, Cl-ABCPA was introduced on the surface of the Si wafers from 1% solution in dichloromethane with a catalytic amount of triethylamine at room temperature under an Ar atmosphere for 2 h. The resulting samples of Si wafers with chemically attached initiating groups were rinsed with dichloromethane under Ar and then with ethanol in an ultrasonic bath. Every step of the modification of the Si wafers was controlled by ellipsometry measurement of the layer thickness. After that the brush was created through graft polymerization described elsewhere.69 We grafted PMA at the first polymerization step and then PSF at the second step using the residual amount of the azo-initiator on the Si substrates. Oxygen was removed from the monomer solution (MA in toluene, 5 mol/L, or a mixture of S and FS in ratio 4:1 wt in THF, 5 mol/L, and AIBN, 4.4 x 10^-4 mol/L) using five freeze-pump-thaw cycles. The Si wafers with the chemically attached azo-initiator were placed into a reactor with the monomer solution under an Ar atmosphere. The reactor was immersed in a water bath (60 ± 0.1 °C) for 12 h. This time of polymerization was determined on the basis of the kinetics of decomposition of the azo-initiator. Relatively slow decomposition of the azo-initiator (half-life of 21 h at 60 °C) allows for the two-step grafting from the surface as has been demonstrated in our previous publications. The Si wafers were rinsed several times with toluene. The nongrafted polymer was removed by cold Soxhlet extraction in THF for 1 h. The same procedure was used to graft the second polymer. The nongrafted amount of the second polymer was removed by a hot Soxhlet extraction in THF for 12 h. Since complete extraction of the ungrafted chains is a critical issue in this system, we have studied extensively the ungrafted polymer extraction with ellipsometry and found that layer thickness does not change significantly after 4 h of extraction time, which indicates complete removal of ungrafted polymers under selected experimental conditions.

Y-shaped polymers were provided by collaborating group of Dr. E. Zubarev.70 After that the standard procedure of "grafting to" approach was applied91 to attach the molecules to SAM layer.
CHAPTER 5

SINGLE MOLECULES FORCE VOLUME MEASUREMENTS

5.1 Procedure

In this chapter the mechanical properties of hyperbranched molecules and their aggregates are discussed. Deposition of molecules was done through absorption see the previous chapter for details. By the date only stretching experiments were done for determining mechanical properties of single molecules.\textsuperscript{57-59}

To collect reliable nanomechanical data, the micromapping of the surface stiffness with a nanoscale resolution should be carefully designed. To enhance the surface stability of the molecular aggregates and provide ideal landscape for the tip-molecule interactions, the dendritic molecules were tethered to an atomically flat silicon surface through an anchoring, amine-terminated, alkyl-silane self-assembled monolayer (SAM).\textsuperscript{71} To avoid high attractive forces, the AFM tips, in turn, were modified with a methyl-terminated SAM.\textsuperscript{18,72}

Characterization and micromapping. Experiments were carried on Dimension 3000 and Multimode, Nanoscope IIIA microscopes. Silicon tips CSC12/50 (NT DMT) were selected for this testing. Spring constants were measured and cross-checked by added mass, tip-on-tip, and resonant frequencies methods.\textsuperscript{73} They usually varied from 0.01 to 1 N/m. Tip radii varied from 10 to 30 nm as measured on gold nanoparticle reference standard. Sensitivity of the piezoelement was carefully measured on a bare silicon wafer right before and after probing. Tapping Mode (TM) images were obtained to identify surface areas with appropriate concentration of anchored molecules. FV micromapping was conducted on several selected locations for selected areas from 200x200 nm to 1000x1000nm. TM imaging was repeated after micromapping to assure preservation of initial surface morphology. Independent measurements of Young's modulus for 40 nm thick spin-coated films from hyperbranched polymers were conducted. FV micromapping was done in a gentle FV mode with pixel-to-
pixel distances of 3-12 nm and local deformation not exceeding 4-6 nm. The tip deflection during the compression cycle was measured for each location and converted to the load-indentation curve. Data were analyzed using Hertzian contact mechanics, a double-spring variable constant model, measured tip spring constants, and tip end shapes to deduce local elastic modulus according to the known procedures and theories. The tip approaching velocity varied to assure that the viscous contribution is insignificant and zooming-out scanning was conducted to assure completely reversible deformation.

Modification of silicon wafers and tips. Additional functionalized of the tips and substrates is required to facilitate nanomechanical measurements. The modified silicon substrates with NH2 SAM layer were prepared for anchoring hyperbranched molecules. Clean silicon wafers were immersed into about 0.015% NH2 SAM solution in ethanol (100%) (2-3 drops of NH2 SAM in 100ml ethanol) for 30 minutes under the condition of nitrogen environment and humidity below 5%. After modification, the substrates were rinsed four times with fresh ethanol (95%) under the nitrogen and once combining with the ultrasonic bath and then dried with a stream of nitrogen at room temperature. Silicon tips were modified with methyl-terminated alkyl-silane SAM to decrease the adhesion between the AFM tip and hyperbranched molecules. Before modification, the tip was put into a small tube and rinsed two times with a mixed solution of ethanol/chloroform (50/50), and then dried with a stream of nitrogen. The clean tips were immersed in 0.015% OTS SAM solution in toluene for 30 minutes under dry nitrogen condition. The modified tips were rinsed two times with toluene and chloroform and two times with ethanol and then dried with a stream of dry nitrogen. N-octadecyl trichlorosilane (for OTS SAM) and (3-aminopropyl)-trimethoxysilane (for NH2 SAM) were obtained from Aldrich and Gelest, respectively, purified by distillation, and separately stored into sealed veils. Spectrophotometric grade toluene was purchased from Aldrich and ethyl alcohol (reagent) and acetone (reagent) were purchased from Fisher Scientific Co. and used as received. All the modification process was performed inside a glove box filled with dry nitrogen under humidity below 5% and under conditions of a class 100 cleanroom.
5.2 Elastic moduli evaluation

Figure 32 demonstrates a typical high-resolution topographical image of two different generations of dendritic molecules tethered to the functionalized silicon. G4 compound formed a random array of individual molecules for a wide range of adsorption conditions as discussed earlier. In contrast, G3 generation dendritic molecules formed a variety of surface aggregates. A number of molecules within aggregates evaluated from molecular dimensions after correction for tip dilation varied from 3 to 40. We observed a coexistence of individual molecules, small round aggregates, along with short-chain and long-chain aggregates as marked in Figure 32. As was demonstrated earlier, G3 molecules form bilayers from compressed molecules within molecular aggregates. G4 compound adsorbed on the solid substrate as predominantly individual molecules with their heights close to a diameter estimated from molecular model. Such surface morphologies correspond to that observed before for regular dendrimers with different levels of flattened conformations for lower and higher generation dendrimers and under conditions of variable molecule-surface interactions.

Figure 32. AFM images (750x750x10nm) of anchored dendritic molecules and their aggregates: G4 (a) and G3 (b). Examples of different aggregates for G3 molecules are marked as follows: I-individual molecule, R-round aggregate, S-short-chain aggregate, and L-long-chain aggregate.
Surface distribution of nanomechanical properties was probed for the randomly selected surface areas containing at least several clusters of different dimensions (Figures 33, 34). Despite some random deviations due to a noise contribution and thermal drift for nanometer displacements probed within a long time period (more than one hour for the highest lateral resolution), a clear correlation can be seen between locations and shapes of molecular clusters on the high-resolution AFM TM image and corresponding topographical, adhesion, and elastic modulus images on FV micromaps (Figure 33). As expected, the stiffness of the aggregates of dendritic molecules and individual molecules statistically was much lower than for the surrounding SAM-terminated silicon surface. Correspondingly, adhesion is higher for the amine-terminated SAM than for the hydroxyl-terminated dendritic molecules as is expected due to stronger amine-hydroxyl interactions when the AFM tip has partially incomplete modification.19

Figure 33. FV analysis of G3 molecular aggregates, 64x64 array, 400x400nm area: topography (top, left) and concurrently obtained surface distribution of adhesive forces (top right) and elastic modulus (bottom).
Several important results were obtained about the mechanical properties of single molecules. All of them were related to the influence of silicon substrate on top layers during compression cycles. During the data processing the simple assumption was made that the first part of the Indentation Load curve has less silicon influence and can be considered as a real data. As a result the distribution of elastic moduli was obtained with three different regions (Figure 35).
A first peak, with high elastic modulus of 1.1 GPa, corresponds to the surface areas of the SAM modified silicon without dendritic molecules. For this type of contacts, elastic response is determined by deformation of alkyl chains of contacting SAMs of the AFM tips and substrates. The value of the elastic modulus obtained is within the range obtained for alkyl-chain containing monolayers with the AFM tips (1-3 GPa).\textsuperscript{31,80} A broad maximum at lower values of the elastic modulus is composed of two peaks. As was identified by analyzing spatial correlation between different histogram regions and surface areas, these peaks corresponded to the central areas of molecular aggregates and the aggregate borders. The absolute values of the elastic modulus for the dendritic molecules within internal aggregate regions were within the range from 100 to 300 MPa. Border regions showed overestimated
elastic modulus values due to the lateral physical contact of the AFM tip and the aggregate edges that increased an actual contact area. On the other hand, the presence of the silicon substrate affects "apparent" modulus in the case when the AFM tip is engaged with aggregate only on peripheral region and the very end of the tip is in the contact with SAM surface (Figure 36). Therefore, for the calculation of the average elastic modulus for the dendritic molecules, we excluded SAM surface contributions and conducted pixel-by-pixel analysis of different aggregates excluding the aggregate edges.

Figure 36. Sketch of dendritic molecules tethered to a silicon surface through anchoring amine-terminated SAM and SAM-modified AFM tip in three different positions during nanomechanical probing: on top of the dendritic molecule, on the border of the molecular aggregate, and on SAM-modified silicon surface (top). Bottom: sketch of various stages of deformation of SAM-dendritic molecule-SAM-AFM tip system. First contact (I), deformation of dendritic molecules (II), further deformation of the dendritic molecules and alkyl-silane SAMs on tip and surface (III), and complete compression of all compliant compounds (IV) are shown from left to right.
The final distribution of elastic moduli with size of aggregates was obtained

![Graph showing elastic moduli distribution.](image)

**Figure 37.** The average elastic modulus obtained for individual dendritic molecules and different types of surface aggregates.

### 5.3 Multilayer Modeling

Conventional models do not give precise solution for the case described above because of the large difference between elastic moduli and as a result the Indentation Load curve consists of several parts that correspond to different compression cases. As initial approach it is possible to use the initial part of the curve for elastic modulus evaluation of polymeric molecules but more precise investigation is done with multilayer model.

As it is possible to observe on FD and Indentation Load curves (see Figure 38, where both slopes are marked by dotted lines) that there are two clear regions with different slopes. The first part after contact point has small slope value and the second part has typical high slope value (usually correspond to interaction between a tip and substrate).
Figure 38. Examples of FDCs for individual G3 and G4 molecules with two different ranges of elastic response (a) and corresponding penetration-load curves (b).
This kind of nanomechanical response is a characteristic of very compliant and thin layer on a stiff solid substrate.\textsuperscript{21,81} Indeed, depth profiles of the elastic modulus presented in Figure 39 for both molecules, possess a characteristic non-monotonic behavior. For G3 molecules, the elastic modulus of around 200-400 MPa is observed for initial 3 nm indentation depth. As can be seen in Figure 39, data points for different molecules are scattered but follow a similar trend. This is followed with a sharp rise, which exceeds the limits of sensitivity (about 3 GPa for this set-up) for the indentation depth higher than 5 nm (Figure 39a).

The height of G3 molecular layer is about 2.5 nm and the total thickness of stiffer, but still compliant SAMs on the AFM tip and on a silicon surface, is about 3 nm. The estimated elastic modulus of SAM layers with alkyl chains is within 1-3 GPa as was shown in several studies.\textsuperscript{82,32} This suggests that they could be compressed under given probing conditions with the average pressure in the contact area reaching 100-200 MPa as estimated from the Hertzian model.

Considering all these circumstances, we suggest a following sequence of elastic deformation processes within the contact area (Figure 36). First, the initial contact involves predominant deformation of the dendritic molecules and an intact state of both substrate and tip SAMs. For very low loads (below 1 nN) and small indentation depth (below 2.5 nm) an elastic compression of the dendritic molecules occurs first. Second, for further deformation (next 2-3 nm of the indentation depth), the dendritic molecules became completely "squeezed". Under higher local pressure, stiffer alkylsilane SAMs on the AFM tip and silicon substrate became subject of elastic deformation themselves. Finally, for even higher normal loads, all organic components became fully compressed and the AFM tip approaches the solid wall, the silicon oxide layer, and further deformation stops. Very similar behavior was observed for stiffer G4 molecules with total elastic deformation reaching 3 nm under similar probing conditions (Figure 39b).
Figure 39. The depth profile of the elastic modulus for G3 (a) and G4 (b). Lines are guides for an eye. Data points are collected for several (3-4) different molecules.

As it was mentioned above the data processing were conducted only for first few nanometers of indentation. The new model allows to improve the values obtained.
Figure 40. a) Typical FDC obtained for molecular monolayer from hyperbranched molecules (G3). Initial part with a low slope (right bottom) corresponds to monolayer deformation. Zero deflection corresponds to the case when any forces do not affect the cantilever. b) Fitting experimental data (empty circles) by the two-layer model (solid line) and Hertzian curve (dot line) drawn for the same value of the elastic modulus.
Overall profile obtained by the fitting procedure reveals the graded model with a very thin (2.5 nm) compliant layer with elastic modulus of 30-80 MPa and the transition zone of 3 nm thick between the polymer monolayer and the silicon substrate as represented in refined model. The results obtained (Figure 40) showed much better data fit comparing with Hertzian model. These values correspond to structural parameters expected for polyester hyperbranched molecules tethered to the silicon oxide surface through epoxy-terminated self-assembled monolayer.  

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CHAPTER 6

BRUSH SYSTEMS FORCE VOLUME MEASUREMENTS

6.1 Brushes in air

6.1.1 Procedure

Brush systems are excellent test system for multilayer model. Because of their unique structure and properties (see Chapter 4) the same sample can provide different combinations of the same components. Depending on the solvent treatment conditions and experimental setup it is possible to receive variety of important cases:

a) Tri-layered systems: these include cases when two or more polymers are placed on a substrate with vertical segregation. Any two component brush system can work for this case after treatment by the solvent that is good for one component and bad for another.

b) Different sequences of stiff/compliant layering will be selected. This can be reached by applying the solvent that is good for one of the polymer components and bad for another. During solvent treatment, the favored polymer component covers the top of the sample. After different solvent treatments, several cases are possible: polymer I or polymer II is on top, or both polymers are found at the top. And after the evaluation of properties of these two different systems we will test the consistency of the results. This case requires special preparations to avoid influence of the substrate.

c) Selection of layers with different ratio of elastic moduli:
   1) Polymer layer/ silicon substrate systems
   2) Glassy polymer/ rubbery polymer systems
d) A top film with different thicknesses for the two layer system can be tested. In this case, the substrate influence can be evaluated. This can be achieved by conducting the experiment in liquid environment.

In this subchapter the mentioned above properties will be investigated in dry environment. Because of the presence of different regions with different properties (Figure 41) the same sample can have different sequences of components after different treatments.

Figure 41. An example of FV data for PSF/PMA brush (1x1 \( \mu \text{m} \)) in case of processing by solvent good for PSF (upper part) and PMA (bottom part). Left column represents morphology and right represents nanomechanical data. Special possible cases are selected by circles when it's possible to suggest the presence of several layers.
Characterization and micromapping. The same as in the previous case the measurements were done on Dimension 3000 and Multimode, Nanoscope IIIa microscopes. Silicon tips CSC12/50 (NT DMT) were selected for this testing. Spring constants were determined from 5 to 15 N/m by tip-on-tip, and resonant frequencies methods. Tip radii varied from 20 to 50 nm and as was mentioned above were measured on gold nanoparticle reference standard. Sensitivity of the piezoelement was carefully measured on a bare silicon wafer right before and after probing. The tip radii measurements were repeated after whole experiment for confirmation that the tip was not broken or contaminated. TM picture of the area was obtained, first, to identify the area on FV picture, and, second, to confirm that deformation was elastic. FV micromapping was conducted on several selected locations for selected areas from 2000x2000 nm to 1000x1000 nm because of the necessity to observe several different domains on the picture to have data for comparison. The tip approaching velocity varied to assure that the viscous contribution is insignificant and zooming-out scanning was conducted to assure completely reversible deformation. Some other experimental aspects should be accounted during mechanical experiments.

First, because of the nanodomain phase separation, high lateral resolution is necessary, which means a very small tip radius must be used. Because of the calibration of the cantilever sensitivity that consists of repeated normal contact with silicon, as well as the repeated indentation into polymer layers, the tip can become blunt and contaminated rather quickly. Accurate FV measurements greatly depend on accurate calibration of the sensitivity, and confirming the constant sensitivity of the cantilever without greatly altering the tip radius is a challenge. Second, PSF and PMA are expected to have contrasting mechanical properties. It has been determined that only a small range of cantilevers, in terms of spring constant and, hence, local pressure, are applicable to probe the surface nanomechanical properties of a given polymer. Since we have a glassy and a rubbery polymer within the same probing area, it is difficult to find a perfectly matched spring constant to probe both. Accordingly, FV probing was repeated several times using stiffer and softer cantilevers to achieve higher sensitivity for either glassy or rubbery surface areas. TM imaging was repeated after micromapping to assure preservation of initial surface morphology.
Theoretical data for bulk materials were found and compared with results from experiments and it was obtained that they correspond to each other.

### 6.1.2 Elastic moduli evaluation

The data obtained were initially analyzed in the way similar to single molecules experiments. The more complex fitting will be done in the next paragraph. Every time when influence of substrate was significant the data analysis was done only on the first part of the curve with assumption that the influence of substrate is minimal there. The several different scans were done with different resolution. The surface histogram of elastic modulus presented (64x64) shows a bimodal distribution of the elastic modulus that is expected for a surface with microphase-separated regions (Figure 42).

![Figure 42. Surface histogram distributions from MMA mapping demonstrating the mechanical difference of the binary brush layer in two separate states. Histograms are taken from 64 x 64 FV scans for a total of 4096 data counts. The elastic modulus is the average value for each data point over the entire indentation range. The histogram representing the modulus in the glassy state shows a bimodal distribution fitted with two Lorentzian functions.](image)

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As it is possible to see the histogram, obtained has several maximums. The main maximum (0.9 GPa) belongs to the component with PSF. It is a typical value for polymers in a glassy state and was confirmed by independent measurements on homopolymer brush. The small maximum corresponds to the case that will be considered separately later when soft material is placed on the stiff substrate. And the range of values around 100MPa corresponds to typical values for rubbery polymers.

Elastic modulus histograms were also obtained using a softer tip (around 5N/m) with higher sensitivity and smaller resolution that allows later to have more data points in Z direction (Figure 43). Softer tip measurements allowed to see more clear phase separation, and larger area that corresponds multilayered systems. Individual measurements are distributed in the range 10-50 MPa (characteristic of PMA domains) and 400-1000 MPa (characteristic of PSF domains and multilayered systems).

Figure 43. FV topography distribution and corresponding elastic modulus histograms from the glassy (top row) and rubbery state (bottom row) using a soft tip. The histogram in the glassy state was derived from the region with the white frame to avoid incorrect data from the damaged surface region. The bimodal distribution is enhanced in the glassy state. Histograms are taken from 32 x 32 FV scans at 1x1 μm.92
6.1.3 Multilayer modeling

As it was mentioned above conventional models can’t describe the situation with substrate present that’s why for the first evaluation the initial parts of the curves were used for elastic modulus calculation.

First, FDCs from the glassy state will be considered. Below there are and examples of FD and Indentation Load curves and distribution of the elastic modulus with depth (Figure 44). The depth profile of elastic modulus distribution for top positions shows uniform distribution during whole indentation. It shows that, first, the layer is relatively thick that’s why tip didn’t reach the substrate and, second, the material is stiff enough to prevent elastic indentation of the tip. In case of bottom points situation is different. The FDCs, Indentation Load curves, and elastic modulus depth profile plots for bottom locations are all characteristic of AFM tip interaction with a rubber on stiff substrate. The indentation occurs till 8nm without visible influence of substrate and after that elastic modulus changed dramatically. As we can see, the influence of the substrate is week in case of top points that’s why the Hertzian model can be used. In case of the bottom points the influence become significant from the depth in 8nm and the model gives the value of elastic modulus as 40MPa.

Another experiment was done for the same brush in rubbery state. The sample was treated by good solvent for rubbery component that’s why almost all top positions represent rubbery polymer. MMA results for the rubbery state are given in Figure 45. FDCs from the “tops” correspond to probing on the weblike structures while “holes” refers to the deep gaps in this structure. For the rubbery state, nearly all FDCs exhibited behavior indicative of a highly compliant surface. Indentation into the PMA was routinely above 30 nm for a load of 50 nN, while for PSF in the glassy state, the deepest indentation was 4 nm for the similar load. Depth profiling of the elastic modulus for the rubbery state showed a steady increase as surface layer was compressed but still did not exceed 70 MPa after 40 nm of indentation (Figure 45). The effect of PSF was felt in the deepest holes as the elastic modulus quickly jumped to roughly 1 GPa after 6 nm of indentation, indicating a thin PMA layer within holes.
Therefore, these results confirm the presence of rubbery PMA layer all over the binary brush after acetone exposure.

Figure 44. Typical FDCs (top, black triangles indicate approaching cycle, gray triangles indicate retracting cycle), load-penetration (middle), and elastic modulus depth profiles (bottom) for the glassy state. Left pictures represent data for the top positions and right for the bottom in Figure 41 for Glassy State.\textsuperscript{92}
Figure 45. Typical FDCs (top, black squares indicate approaching cycle; gray squares indicate retracting cycle), load-penetration (middle), and elastic modulus depth profiles (bottom) for the rubbery state. “Tops” and “holes” correspond to MMA probing on the PMA weblike structure and PSF dominated surfaces in the 100 nm deep holes, respectively, in Figure 41 for Rubbery State.92
The same as in glassy state the top points doesn’t have significant influence from substrate but bottom point are the rubber part on silicon or PSF and the model gives the same number 40MPa for this case.

6.2 Brushes in a solvent

6.2.1 Procedure

An example is presented for application of the approach, described here, to a complex case of a very complaint polymer layer grafted to a solid substrate and placed in selective solvent. AFM experiments were done according to the experimental procedures described elsewhere. Spring constants were selected in the range from 0.1 to 0.4 N/m depending on sample elasticity and measured according to described technique. The blunt tips with radius 40-50nm were selected for the experiment. Experimental force-distance data (cantilever deflection versus piezoelement displacement) collected in the FV mode were processed by MMAnalysis software package developed in our laboratory with an added option for the multilayered analysis.

Polymer brush layers are composed of macromolecules chemically grafted to a solid silicon substrate through a mediating functionalized self-assembled monolayer (Figure 46). In the case considered here, a binary polymer brush layer was prepared from rubbery poly(acrylic acid) (PAA) and glassy poly(styrene) (PS), both with high molecular weight, grafted to a silicon wafer by the “grafting to” approach as described elsewhere. An array of FDCs was collected for the surface areas of 0.7 x 0.7 µm. Surface topographical images were obtained before and after the experiments to confirm that deformations were elastic.

An example of the FDC for the binary polymer brush (PS/PAA) placed in a good solvent for PAA (water) is presented in Figure 47. Under this solvent, polymer chains were highly swollen and possessed very low elastic modulus as expected for polymers in a good
solvent. Under these conditions, FV probing with very low normal forces generated an array of FDCs with a complex shape showing two regions with different slopes.

![Diagram of polymer brush layer with polymer chains tethered to the solid substrate via SAM.](image)

**Figure 46.** A general sketch of Y-shaped polymer brush layer with polymer chains tethered to the solid substrate via SAM.

![Graphs of cantilever deflection and indentation.](image)

**Figure 47.** a) An experimental average loading FDC obtained for the system under water on stiffer surface for Y-shaped binary brush layer. b) Fitting the experimental loading curve (circles) by the two-layered model (solid line).
Accordingly, the loading curve with the indentation depth reaching 6 nm displayed a complex shape, which deviated significantly from normal Hertzian behavior expected for a uniform elastic material (Figure 47). Individual FDCs had similar shapes with higher level of noise removed by the averaging of a significant number of experimental curves.

After that the same experiments were done in a good solvent for the second component (PS), in toluene. Figure 48 represents FDC for this experiments and Indentation Load curve.

Figure 48. Left: An experimental average loading part of FDC obtained for the system under toluene on stiffer surface for Y-shaped binary brush layer. Right: Indentation Load curve.

You can see that FDC doesn't have jump to contact that removes initial distortions. The second feature is that the loading and unloading parts absolutely identical that shows the absent of adhesion forces. Another difference from usual multilayer systems is that the Indentation Load curve is almost linear. This fact allows to say that the substrate influence is not significant.
6.2.2 Elastic moduli evaluation

Two different cases of elastic modulus evaluation is considered here. The first case covers the situation when a substrate influence is significant. PAA in a swollen state is an extremely soft material. The substrate influence becomes significant after the first 5 nm of indentation, and that is why a multilayered model with two layers was applied. The best fitting of the loading curve and the depth profile can be obtained by using a very low elastic modulus value of 9 MPa for initial deformations not exceeding 6 nm. This very compliant region is replaced with rising elastic resistance for larger indentation depths caused by the presence of the underlying solid substrate (Figure 49).

![Elastic modulus vs Depth](image)

**Figure 49.** Fitting the experimental data on the depth distribution of the elastic moduli of polymer layer in toluene (circles) with the two-layered model (solid line).

In case of PS, as it was mentioned, the nanoprobe did not reach the substrate and that is why conventional Hertzian modeling gives reliable results. The measurements of elastic modulus give a value around 3 MPa. The swollen brushes are gel-like and the calculated data for both states show significant decreasing in elastic moduli in respect to the dry states.
CHAPTER 7

GENERAL CONCLUSIONS

The nanomechanical properties of materials consisting of layered responsive brushes down to individual molecules become more important with the growing development of nanodevices. AFM provides a unique tool for analysis of these properties. Only a few experimental studies have been done that apply AFM as a device that can give necessary information and develop theory for describing AFM/sample interaction, and previous models developed around AFM fail to correctly recognize the substrate influence in the cases described in this thesis.

That is why it was critical to develop a model that can describe the process of nanoindentation for different systems as collected with AFM. A model has been derived and it has several important properties. In addition to the fact that a theoretical model can repeat an experimental Indentation Load curve and a distribution of elastic moduli with depth, it was also shown that it can predict the indentation behavior for different ratios between elastic moduli of the layers and the thickness of interfacial zone when the AFM measures influence from both layers (effective modulus). All of these factors make the model a unique tool for nanoindentation behavior prediction. In addition, it can give some interesting prediction for elastic behavior of four and more layer systems that could not be measured previously due to different limitations.

Regarding the software development, the model was implemented as an independent block in an already pre-existing development to give the choice to compare model prediction with Hertz/Sneddon behavior. An important development was done for data preprocessing. In fact, there are many contributions that can disturb the experimental FDC but indeed are below the AFM sensitivity and are the result of some different factors. Now an operator has a choice to do data smoothing before mechanical analysis and after. It was shown above that data smoothing allows to predict a number of layers for multilayered models. As independent
block several viscoelastic models were built in to compare theoretical behavior with experimental and evaluate the contribution of viscoelastic factors.

The last step was the experimental part. Completely new measurements for single molecular stiffness measurements were conducted for individual hyperbranched polyesters. By the date only stretching experiments were done for single molecules to evaluate different properties of them. It was shown that during the compression cycle the substrate influence becomes significant and the multilayered model should be used. It was obtained that the values of elastic moduli for single molecules and their aggregates are in the range of 100-300MPa. Another important fact observed was that data obtained depended upon the landing position of the tip. It was shown that if the landing occurs on the border between a molecule or molecular aggregate and substrate, simultaneous deformation takes place. That is why it was necessary to select only data points when pure molecular compression happens. Other experimental tests were conducted on brush systems. As was mentioned above, these systems have an excellent property to switch the state under different solvents treatment. The set of polymer brushes were selected when one component is in a glassy state and another one in a rubbery state. The systems were investigated after different treatments in air environment and the data obtained were close to the results from bulk materials. Y-shaped polymer brushes were tested under fluid environment also, and the results from the model fitting showed that they are significantly smaller if we compare them with data from dry states.

In conclusion, in the course of this work, the model was developed that can be used for nanoscale mechanical analysis on unique polymer systems. The model was tested on different polymer systems and it was shown that a set of important parameters can be obtained. In addition to the model development, experimental measurements were done for several selected systems. All of these systems have their unique properties that can be used for different applications and all of them required unique experimental setup and data processing to obtain reliable results.
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