Single Molecule Force Spectroscopy of Siloxanes

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Abstract. Silicone elastomers are high tech materials with some disadvantages. In order to make some improvements, the measurement and analysis of force-extension curves with Single molecule force spectroscopy (SMFS) is necessary. To determine the elastic properties of the silicone elastomers, modifications on the cantilevers and on the wafer surfaces have been performed.

1. Introduction
Silicone elastomers are high tech materials with many applications [1]. But they have also some disadvantages, such as, low tear strength [2]. In order to make some improvements, deeper understanding of the fundamental processes is necessary.

Single molecule force spectroscopy (SMFS) is a great scientific method to directly access single molecules at the nanometer scale. It is possible to detect and interact with individual molecules or even atoms on surfaces [3, 4].

Main focus of this thesis is the measurement and analysis of force-extension curves. In doing so it was managed to determine the elastic properties of the silicone elastomers. Modifications on the cantilevers and on the wafer surfaces have been performed in this practical course.

During the experiment procedure, the polymer chains were pulled out of a solvent. The necessary force could be measured directly, as peaks in the force-extension curves. By measuring the molecules were not totally linear, so at first, entropic forces had to be applied to linearize the polymer chains. To further stretch the molecules, higher forces were required, which could overcome the enthalpic forces and extend bond angles and lengths.

2. Experiments

2.1. Preparation Method
1cm × 1cm, cleaned in 2% Hellmanex II detergent in HPLC-pure water, washed with copious HPLC-pure water, then washed with HPLC-pure methanol and acetone, stored in pure HMDS and dried under nitrogen before use. Modified surfaces were made by immersing a piece of washed SiO2 wafer into 2.5mL 0.1% PDMS solution (Polymer HCl 950) for overnight before use. Before the measurement, 4µL catalyst was added into the sample solution on the wafer. Normal cantilever from Park Scientific Inc., washed with pure HMDS, stored in pure HMDS and dried under nitrogen before use. Modified tips were made by immersing a washed cantilever into 1mL 0.1% PDMS solution (Polymer HCl 950) with 4µL catalyst in it for an hour before use. The measured sample solution for this experiment was directly from Wacker-Chemie GmbH.
2.2. Calibration of the Cantilever

The MFP might be used with a variety of cantilevers, which have a gold-coated back to increase laser reflectivity. Specific application and sample determined which type of cantilever should be used. For this experiment only the silicon nitride cantilevers of the contact microlever (MLCT-AUHW P/N 00-103-0925) were used. There were 6 V-shaped tips on the cantilever chip and the second biggest one with a height of about 3 µm and a typical curvature radius of less than 40 nm was suitable in our case (Figure 1).

To convert the measured voltage signal from the photo-detector into a force in Newton, the cantilever must be first calibrated. Depending on the position of the laser spot, the deflection signal will be more or less sensitive towards forces applied on the tip [5, 6]. This sensitivity (i.e. the change in deflection signal for a given cantilever curvature) is called also Inverse Optical Lever Sensitivity (InvOLS) and has the units of mV/µm. to measure the sensitivity (S), a glass cover slip with a fluid sample droplet was used. First the cantilever was pressed into contact with the surface and a short force curve of the sample indentation was measured. Then the sensitivity was calculated based on the slope of the curve, when the cantilever touches the surface of the glass cover slip [7].

The next step was to determine the cantilever spring constant k, which was calculated according to the thermal oscillation method [8, 9]. By approximation, the cantilever could be described as a Hookean spring.

\[ F = - kx \]  

According to the equipartition theorem, each degree of freedom in a thermodynamic system is assigned the same thermal energy [10]. Therefore a freely swinging cantilever mode will be excited with the energy E.

\[ E = \frac{1}{2} kBT = \frac{1}{2} k<x^2> \]  

Where k is the spring constant and \(<x^2>\) is the time average quadratic amplitude of the cantilever thermal fluctuation.

The direct determination of the time average quadratic amplitude of the free spring \(<x^2>\) is not possible because of the electrics or the other environmental noise. Therefore the cantilever is oscillated at different frequencies and the value is conveniently determined by integration of the harmonic oscillation peak in the frequency domain of a power spectrum [11, 12]. At the resonance frequency of the cantilever the measured spectral density [pN²/Hz] has a maximum and the maximum can be determined by a Lorentzian fit (Figure 2).
And then the value of the maximum can be transformed to the time average quadratic amplitude $<x^2>$ with the following equation, which is derived from Fourier transformation of the time dependent function.

$$<x^2> = \lim \left( \frac{1}{t} \right) \int x(f) X(f) \, df$$  \hspace{1cm} (3)

Where $X(f)$ is the $x$ function of $f$ at the resonance frequency.

Although the frequency $f$ is already known by data of the manufactures, this method was used to confirm that the system is functioning correctly [13, 14]. Furthermore there could be big differences in spring constants for different batches of cantilevers [15]. The spring constants $k$ of the used cantilever in this experiment were always determined to lie in the range between 45 and 60 pN/nm.

Finally, by bringing the two calibration constants together, the photo-detector deflection signal $A$ in volts can be converted into a force value.

$$F = k \frac{A}{S}$$  \hspace{1cm} (4)

2.3. Measurement

Before the calibration of the cantilever, a drop of sample solution was added between the cantilever tip and the surface of the wafer on the glass cover slip to form a fluid droplet. Since the sample solutions evaporated within a few ten minutes, this procedure had to be repeated during the experiments. The pulling velocity of this experiment was 2µm/s and however, the hydrodynamic drag at this velocity was so high that a shift between approaching and retracting graph can be seen.

2.4. Analysis

After the force curves were baseline corrected and had been transformed into tip-sample distance-force curves, the analysis of the force curves with Langevin events was performed with the software package program.

Since thousands of force curves had to be measured, a program was needed to speed up the analysis. With a procedure program, the analysis time was reduced strongly. The procedure created the new item “Peak Analysis” in the main menu. The button opened a window. With the “all in one” button a horizontal line fit was created between the two cursors, which should be positioned at the beginning and
the end of the plateaus. The values were printed into a table, which consists of the column suffix of the waves, the lengths and heights (force) of the rupture event, etc..

3. Results and Discussion

This Chapter presents the observed typical stretching force curves of siloxanes. Although the wafers and the cantilevers were chemical modified in the experiments, polymer chains could not attach to the cantilever tip so simply. That is to say, in the most case there was no force peak in the measured force-extension curves. So normal force curves (Langevin events) were very rare and a wide distribution of pulled molecule lengths was measured. These force curves could be fitted with the WLC model. The entropic and enthalpic elasticity parameters such as spring constants could be determined from these fits. The whole practical course was divided into two different parts: the modification of the cantilevers and the modification of the wafer surfaces.

![Figure 3. Typical force curve for siloxanes.](image)

Figure 3 is a typical directly measured force curve from Igor program. According to the analytical data, the observed maximum rupture force was $6.353 \times 10^{-10}$ N and the maximum contour length was $1.556 \times 10^{-7}$ m. This is consistent with the formerly measured Si-O bond strength (0.6-0.7 nN) and the average polymer length of 154 nm for 950 units (the bond length of Si-O is about 0.162nm). Unfortunately, some of the resolutions of the measured data are not always sufficient to determine the molecular fitting parameters accurately. A fit with the extended WLC function is also valid in the range of very low and high forces.

When the experimental data were analysed with the Origin program, all of the data should be modified at first. Since the spring constant of the single molecule is more than 0.15, only the data with suitable spring constants could be applied. After the modification of the data, the molecular lengths and the rupture forces were statistical normalized. Using the Lorentzian fit or the Gaussian fit, the mean of the molecule length and the rupture force could be achieved.
Figure 4. Histogram of the siloxanes rupture forces.

Because of the very wide data distribution, this histogram of the rupture force (Figure 4) can not be fitted with the Lorentzian or the Gaussian function very well, but in it two maximum peaks can be observed. One of them is approximately 0.2 nN and the other is about 0.7 nN. 0.2 nN is much smaller than the Si-O bond strength and 0.7 nN is in agreement with the formerly measurement. The reason for the first peak (0.2nN) is probably the break between the polymer chain and the cantilever tip or the wafer surface. That means, before the rupture of the Si-O bond, the attachment between the polymer chain and the cantilever tip or the wafer surface has already broken down. In this histogram, several nN forces were also observed. By the same token, two maximum peaks can be observed in the histogram of the single molecular length, which can not be fitted well with suitable function either (Figure 5).

Figure 5. Histogram of the siloxanes rupture lengths.

The first peak of about 50 nm is, like the first one in Fig. 4, because of the break between the polymer chain and the cantilever tip or the wafer surface. The second peak of approximately 500 nm is much longer than the single molecular length, which was with the theoretically calculation 154 nm.
4. Conclusions
The main focus of this thesis is the measurements of the bond strength and the bond length. To examine changes in the molecule’s elastic properties, it would be necessary to keep a polymer molecule attach to the cantilever tip during successive stretching cycles. But unfortunately these reversible pulls could not appear in this experiment. When the pulling distance is shorter than the molecules contour length, these occasions maybe happen.

From Figure 4 and 5, it could be observed, although during the experiments the catalyst was applied to make the polymer chains attach to the cantilever tips or the wafer surfaces stiffly, most of the stretching events was caused by the case, that the siloxanes fell off the cantilever tips before their finally rupturing.

Low signal to noise ratios and pulling geometries can all influence the measured elasticity parameters and cause the error in the SMFS spectroscopy.

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