Good Practice Guide No 3 of the EMPIR project MicroProbes

Measurement of Liquid Lubricant Layer Thickness Using the Force-Distance Curve Method with Fast Microprobes

Sebastian Friedrich, Brunero Cappella

Federal Institute for Material Research and Testing (BAM), Unter den Eichen 87, D-12205 Berlin, Germany

Introduction

Polymeric lubricants form thin films on solid substrates and are employed to reduce friction and wear. With AFM force-distance curves (FDC), the thickness of such films can be determined down to some nanometers [1-3]. When the tip approaches the lubricant film, a meniscus is formed, which causes an attractive capillary force. This capillary force *F*(*H*), where *H* is the distance between the tip apex and the three-phase contact line, is caused by the surface tension γ and is given by

$$F\ (H) = p(H)\gamma \sin\alpha, \qquad (1)$$

with the perimeter of the three-phase contact line *p*(*H*). The angle α is given by $\alpha = \frac{\pi}{2} + \beta - \theta$, where β is the half aperture of the tip cone and θ is the contact angle between lubricant and tip. Hence, the force acting on the cantilever depends on the shape of the tip, the surface tension, and the contact angle between lubricant and tip.

The retraction curves can be used to analyze properties like adhesion and pinning. Because of pinning of the three-phase contact line and stretching of the meniscus, the retraction curve is usually much longer than the approach curve. Additionally, the lubricant often climbs up the tip while it is immersed. Therefore, only the approach curve can be used to determine the film thickness. The thickness of the lubricant layer is calculated as the difference in piezo extension between the jump-to-contact and the onset of the repulsive force, plus the cantilever deflection at this onset. The significant points are shown in an exemplary force-distance curve on the polyolester Emkarate in Fig. 1.

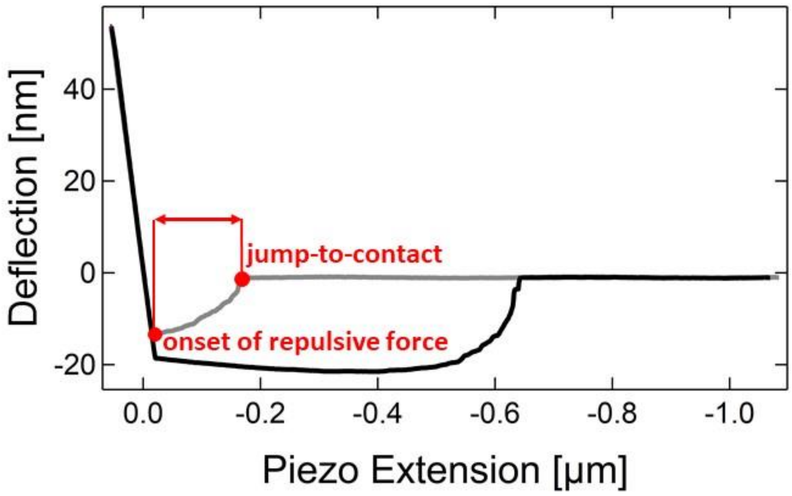

Fig. 1. Exemplary force-distance curve on the polyolester Emkarate highlighting the significant points for the determination of thickness. The approach and retraction curves are displayed in grey and black, respectively.

Experimental Details

Sample Preparation

A droplet of lubricant was put on a glass slide, which had been previously rinsed and cleaned with acetone. The droplet was then wiped off with another piece of glass slide, or with a Kimwipe, so that the remaining lubricant formed a film with thickness in the nano- to micro-range.

Experimental Setup

Experiments were conducted on a Cypher AFM (Asylum Research, Oxford Instruments, Santa Barbara, USA) with a custom-built holder for a piezoresistive microprobe. A piezoresistive wheatstone bridge is located at the clamped end of the cantilever. The deflection signal from the wheatstone bridge is amplified and fed to one of the *holder input* channels of the AFM. Further details of the custom probe can be found in Ref. [4]. The holder in its transport box is shown in Fig. 2 (taken from Ref. [4]). A CAN50-2-5 microprobe (CiS Forschungsinstitut für Mikrosensorik GmbH, Erfurt, Germany) with a length of 5 mm, a width of 200 µm, and a height of 50 µm was used. A monolithic silicon tip (height: 100 µm, cone angle: 45-50°) was located near the free end of the cantilever. Additionally, a CAN50-2-5 microprobe which was shortened to 3 mm to increase its spring constant has been used. On the shortened probe, a diamond tip has been attached instead of a silicon tip.

Experimental parameters like the tip velocity or the maximum force (trigger point) can be chosen at will because they do not affect the approach curve.

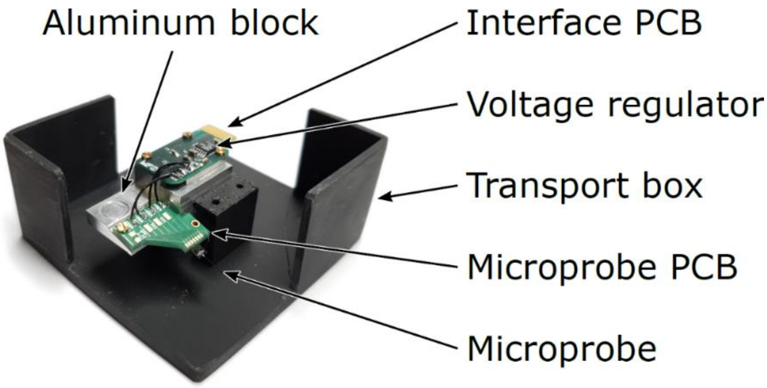

Fig. 2. Custom microprobe holder comprising an aluminum body and two PCBs to operate a CAN50-2-5 microprobe in a Cypher S AFM [4].

Thickness Measurement

A force volume measurement, i.e., a rectangular array of FDCs with well-defined spacing in between single curves, allows mapping of the lubricant film thickness. Figure 3 (taken from Ref. [4]) shows a thickness map of a film of Lupranol VP 9209 (from BASF, Ludwigshafen, Germany), a perfluoropolyether. The map is extracted from a force volume with 50x50 FDCs on an area of (30 µm)². Additionally, a line profile through the thickness map is shown. The tip used in this measurement was already rather blunt from previous measurements and had the shape of a truncated pyramid or cone. The spacing between two subsequent FDCs is 600 nm, which is less than the width of the apex of the tip. However, the borders of the liquid film can be detected quite well. The film has an average thickness of 90 nm, which is near the upper limit that can be detected with the CAN50-2-5 cantilever for this lubricant.

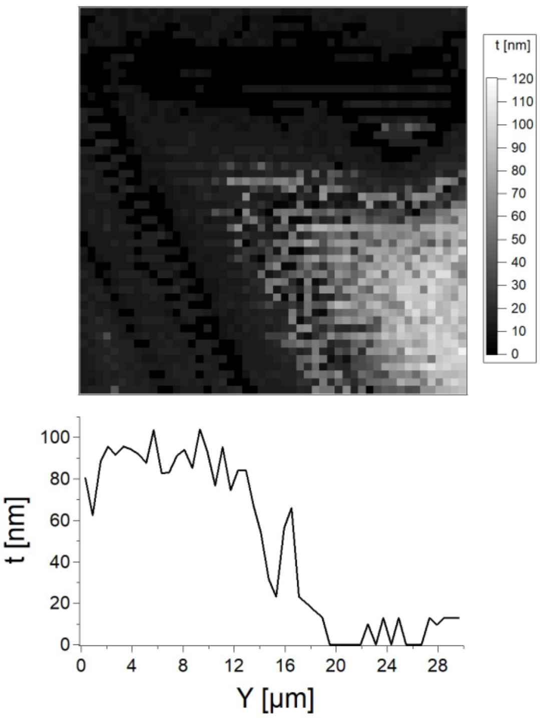

Fig. 3. Thickness map and a vertical line profile at X=27.8 µm of a Lupranol film, measured with a sensor of 5 mm length [4].

Limitations and possible errors of the method will be discussed in detail in the next section. One method to extend the measurement range is to increase the spring constant by using shorter cantilevers. With the cantilever which has been shortened from 5 mm to 3 mm, measurements could be performed on a Lupranol film with a maximum height of 800 nm and a lateral spacing of 500 nm, as shown in Fig. 4.

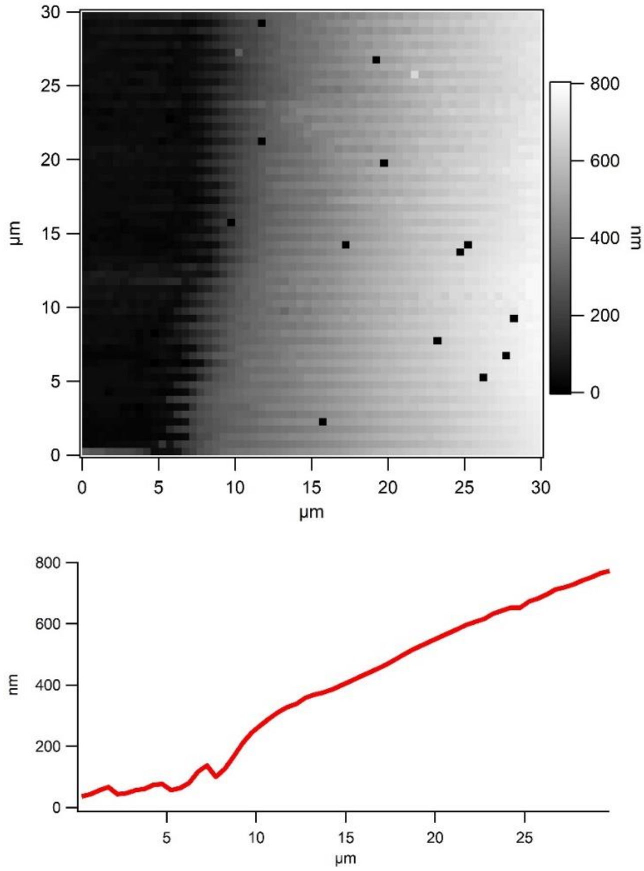

Fig. 4. Thickness map and horizontal line profile at Y=15 µm of a Lupranol film, measured with a sensor shortened to 3 mm length.

Errors and Limitations

Tip Contamination:

In between single FDCs, some of the lubricant can remain on the tip. By comparing AFM with ellipsometry data, Mate *et al.* have shown that this can result in an overestimation of the film thickness by a few nanometers [1]. For films, which are significantly thicker than that, this error is negligible.

Film Deformation:

Since there is an attractive van der Waals-force between tip and lubricant film, the cantilever bends downward and the tip snaps into contact with the film, while the film deforms towards the tip. For a stiff cantilever, the deformation of the film is more significant and leads to an overestimation of the film thickness. However, measurements with cantilevers of different stiffness (0.3 – 63 N/m) on a droplet of the perfluoropolyether Fomblin (Sigma Aldrich, St. Louis, USA) did not show any systematic dependence of the measured film thickness on the cantilever stiffness [2]. Therefore, this error can be considered negligible as well.

Long Retraction Curves

Retraction curves before the jump-off-contact from the liquid can be significantly longer than the respective approach curve between jump-to-contact with the liquid and the onset of the repulsive force. There are two reasons for this:

- Most lubricants climb up the tip once it is in contact with the film. Therefore, the height *H* of lubricant on the tip (distance between tip apex and three-phase contract line) can be much larger than the film thickness in its rest position.
- For most lubricants, the three-phase contact line shows pinning to the tip. This means that, when the retraction starts, the three-phase contact line does not move initially, but only after a certain maximum force is reached (see Fig. 1).

Because of those two points, the tip has to be retracted by a distance that is significantly larger than the film thickness until the meniscus breaks. Yet, the maximum distance by which the tip can be retracted is limited by the Z Piezo range (6 µm in a Cypher). A force volume can only be recorded if the tip can be retracted far enough for the meniscus to break at each point.

For a given lubricant, this limits the maximum film thickness that can be detected. This limit is higher for lubricants which do not significantly climb up the tip, or are even pushed back by the tip, i.e., where *H* is not much larger or even smaller than *S*. This is the case for Lupranol, the lubricant examined above.

Another way to limit the capillary force and thereby extend the measurement range for the film thickness is using sharp tips with a small opening angle. This reduces the diameter of the three-phase contact line. The tip in the example was, unfortunately, very blunt.

Additionally, using cantilevers with a large elastic constant increases the measurement range, as shown in the section above. The use of such short cantilevers also allows measurements on Lubricants which, in contrast to Lupranol, climb up the tip, such as Squalan or Halocarbon Oil.

Acknowledgement

The 17IND05 MicroProbes project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation programme.

Literature

[1] Mate CM, Novotny VJ, Molecular Conformation and Disjoining Pressure of Polymeric Liquid Films, J. Chem. Phys. **94** 8420-8427 (1991)

[2] Cappella B, Force Distance Curves on Lubricant Films: An Approach to the Characterization of the Shape of the AFM Tip, Micron **93** 20-28 (2017)

[3] Friedrich S, Cappella B, Study of Micro- and Nanoscale Wetting Properties of Lubricants Using AFM Force-Distance Curves, Tribol. Lett. **68** 36 (2020)

[4] Fahrbach M, Friedrich S, Behle H, Xu M, Cappella B, Brand U, Peiner E, Customized Piezoresistive Microprobes for Combined Imaging of Topography and Mechanical Properties, Measurement: Sensors (2021)