APPLICATION OF NANOSCALE MEASUREMENT PRINCIPLES AT MICROSCALE: ADHESION AND INDENTATION EXPERIMENTS ON VISCOELASTIC MATERIALS

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1 Introduction

Surface characterisation of materials at the nanoscale is commonly done using an atomic force microscopy (AFM). Adhesion (or surface energy) and mechanical properties like hardness and Young’s modulus are reported in AFM studies by the tip-sample response obtained as an “approach-retraction curve” or “force-distance curve” [1]. Using the same approach-retraction principle but at the microscale, it is possible to quantitatively characterize surface properties of some viscoelastic materials like greases and polymeric materials which often are difficult or impossible to characterize with the AFM.

In this paper, we demonstrate the procedure to measure approach-retraction force curves at the microscale with a force resolution of 0.2 µN. This principle was successfully applied and is illustrated here for two cases: indentation of viscoelastic polymers and properties of greases. On greases it was possible to quantitatively differentiate various grease types, as well as those varying in thickener content. Using the same approach-retraction principle, the hardness characterisation of polyurethane based polymers was done. Quantitative data obtained through such indentation experiments were consistent with macroscopic conventional test measurements which validates this novel micro range experimental approach.

2 Experiments

The test methodology consists of performing approach-retraction experiments using a spherical probe (a ball) attached to a flexible cantilever. A microtribomenter (Falex MUST®) was used for these experiments [2]. The ball is moved towards a surface (approach) and compressed with a known load. Later the ball is moved away (retraction) from the surface. During this approach-retraction cycle, the tangential force on the cantilever is measured as a function of time and distance moved. This technique is somewhat analogous to pull-off force experiments done with an atomic force microscope at nanoscale in order study physical interactions between various surfaces [1]. The choice of the experiment -adhesion or indentation- depends on the counterbody (steel ball or a diamond tip) and the stiffness of the force detection element (a cantilever and fibre optic sensor). Two types of viscoelastic substances were chosen for this study, namely lubricating greases (Supplied by Dow Corning, DE) and Polyurethane based polymers (Supplied by Recticel, BE).

![Fig. 1. Experimental procedure for approach-retraction experiments](image)

3 Results and Discussion

During approach-retraction experiment, the total distance moved by the motion table ($d_{LMS}$) will be equal to the deflection of the cantilever ($d_{cantilever}$) plus the accommodated distance within the material depending on the overall contact stiffness (type of viscoelastic substance) as shown below,

$$d_{LMS} = d_{cantilever} + d_{visco} \quad (1)$$

where

$$d_{cantilever} = \frac{F_t}{K_f} \quad (2)$$

$K_f$ is stiffness of the spring. On combining (1) and (2) the displacement (strain component) within the material can be calculated as,

$$d_{visco} = d_{LMS} - \left(\frac{F_t}{K_f}\right) \quad (3)$$

3.1 Characterisation of Lubricating Greases

A typical tangential force on the cantilever versus the motion table displacement during an approach-retraction experiment is shown in Fig. 2. This curve can
be divided into three segments yielding useful information about the grease.

During approach, the ball comes in contact with the grease. The ball encounters some resistance from the viscoelastic grease. The area represented as section A in the Fig.2 is amount of work required to overcome the resistance of the grease or work done for compressing certain volume of grease. On retraction some additional force is required to counteract the interaction force of the grease and start physically separating the ball from the grease. This interaction force is a competition between the adhesion force (ball-grease) and cohesion force (grease-grease). When the maximum deflection on the cantilever in +X direction is multiplied by its spring constant, the additional force known as ‘pull-off force’ is obtained. Thus work of separation or pull-off work can be represented as section B (Fig. 2b). Although pull-off marks the onset of separation, the eventual release or physical separation of the ball and greased contact is dictated by the grease threads (or meniscus like structures). The meniscus structures or so called tackiness is one of the characteristic of lubricating grease. The grease threads decelerate the release rate which causes a non-linear section in the retraction curve after pull-off point (Fig. 2). The section that determines the energy required to break these grease threads is denoted by section C in Fig. 2b.

![Fig 2. Typical approach retraction curve obtained on a grease](image)

The effect of grease microstructure on its properties was studied on three greases. The first being a Lithium Soap thickened material without solid lubricant additives based on Silicone oil – hereafter referred as GREASE. The second being a partially Lithium soap and partially Solid Lubricant thickened material based on mineral oil referred as GREASEPASTE. Lithium Soaps build a network of fibres that act like a sponge holding the oil, typical greases contain in the order of 3-7 weight percent of Lithium Soap depending on manufacturing process and base oil viscosity/type. The third being a Solid Lubricant thickened material based on mineral oil - PASTE. Solid Lubricants only thicken oils at weight percentages above 30, comparable to wet sand with the difference that particle sizes are in the 2-10 micron range. Two types of industrially relevant substrate materials namely steel and polyoxymethylene (POM) polymer were chosen for this investigation. A bearing steel ball 3 mm in diameter (Stainless steel ISO 3290 grade) was chosen as the counterbody. A thin layer of grease approximately 200 µm thick was applied to the substrate using a spatula.

![Fig. 3. Approach-retraction curves recorded on different greases applied on steel substrate](image)
exhibited unstable oscillations (damping signal in Fig. 3b) at the pull-off point which indicates low tackiness of the grease. This quantitatively proves that grease can be sticky but not necessarily tacky. The PASTE was the odd one out in the sense that the work of separation was very small compared to other greases. The tackiness energy or energy to break grease threads measured on the three types of greases is also shown in Fig. 4c. The GREASE shows highest tackiness (10 times higher than other greases) whereas GREASEPASTE and PASTE have almost no tackiness.

A unique pop-in phenomenon during the approach was noticed in the case of PASTE (Fig. 5). During first adhesion cycle, the steel surface is clean. The micro-sized particles in PASTE have an affinity towards metallic surface due to electrostatic forces which is reflected in the form of a pop-in of magnitude 100 µN during approach (see cycle 1 in Fig. 5). However after the first cycle, there is a transfer of grease on to the steel ball. As expected, due to particle-particle interaction from the second cycle, a large pop-in feature (up to 400 µN) is noticed at 50th cycle. This finding illustrates the sensitivity and precision of this test technique.

**Fig. 4**. (a) Energy of compression (b) pull-off work (c) Tackiness energy recorded on the tested greases

Quantifying interaction properties of grease which has slight variations in thickener content is often difficult. In order to study the effect of thickener content on grease characteristics, two variations of GREASE low (low thickener content) and GREASE high (high thickener content) were considered. Typical characteristic approach-retraction curves for these two greases are shown in Fig. 6a. On using eqn. (3) on the loading part of the curves shown in Fig. 6a, a plot of contact load versus distance accommodation within the grease can be plotted as shown in Fig. 6b. The load bearing can also be related to the amount of network structure which again is a function of thickener content. Grease with high-thickener content would give large resistance to the ball than low-thickener grease. For the same distance accommodation of 0.26 mm, GREASE high gives a resistance force of 10 mN whereas GREASE low a resistance force of 3.8 mN (see Fig. 6b). Thus GREASE high exhibits a stiffness of 38.46 N/m and GREASE low 14.62 N/m. This measurement correlates well with the conventional cone penetration data on these greases: the cone-penetration number [3] for ‘GREASE high’ is 240–280, and for ‘GREASE low’ it is 290-330 which also means GREASE high is stiffer than GREASE low.
3.2 Mechanical characterisation of Polymers

Some industrial polyurethane based polymers were characterised using the same approach-retraction experiments. The polymers were designated as UER 02/01, UER 02/03, and UER 02/05 which differ in the extent of cross-linking. For this measurement, a Berkovich diamond counterbody and stiff 5200 N/m cantilever were used. The approach-retraction tests are therefore analogous to indentation experiments where the main objective is to physically deform the material. For the indentation tests, the indenter was compressed on the material until a target load of 1000 mN was reached. The load was held constant for 30 seconds and then retracted. The result of the approach retraction cycles on three polymers after extracting the true displacement within the material (eqn. 3), are shown in Fig. 7. The approach retraction experiments were carried out at 0.05 mm/s speed.

Both UER 02/01 and 02/05 creep during the 30 s waiting period (constant load of 1000 mN was applied). The drop in the applied load is indicative of sink-in of the polymer material. To justify these measurements, some indentation experiments were carried out using commercial nanoindenter (CSM Instruments®, Switzerland). Even in these tests creep behaviour was noticed on UER 02/01 and UER 02/05 indicated by a drop in the applied load was noticed (Fig. 8).

Fig. 6. (a) Typical approach-retraction curve on GREASE high and GREASE low applied as 100 µm thick layer (b) Contact load versus distance accomodation in GREASE high and GREASE low

Fig. 7. Indentation curves on UER 02/01, 02/03, 02/05

From the shown indentation curves in Fig. 7, quantitative information on hardness can be gathered by measuring the residual plastic depth and total...
penetration depth for achieving the target load. A summary of the micro-indentation experiments is given in Fig. 9. UER 02/05 has the highest hardness as it records lowest plastic deformation depth and total depth of penetration. UER 02/01 seems to be the softest. The ranking in decreasing hardness is UER 02/05 > UER 02/03 > UER 02/01. The obtained results were also compared with conventional shore hardness-A data as well as the data from nanoindenter obtained by ‘Oliver-Pharr method’. The results obtained in this study through approach-retraction tests correlate well with shore hardness trend (see Fig. 9) whereas partly with the nanoindentation data which exhibits no difference between UER 02/01 and UER 02/03 (Fig. 9). The relevance of nanoindentation experiments on such soft polymers is arguable as discussed in some of the recent studies [4]. Thus the measured effects correlate well with macroscopic hardness test data on polymers.

![Fig. 8. Nanoindentation tests on UER 02/01 and UER 02/05 using a commercial nanoindenter. Maximum load = 5 mN, Loading and unloading rate = 10 mN/min, Holding time= 5 s, Oliver-Pharr method.](image)

![Fig. 9. Summary of indentation tests and comparison with conventional shore hardness test on polymers](image)

4 Conclusions

- Effects known in atomic force microscopy technique or approach retraction experiments can be successfully translated at microscale for gathering useful quantitative data on structure-property relationship of viscoelastic materials like greases and polymers.

- The proposed technique is capable of distinguishing greases with subtle differences in the microstructure within µN range precision. The phenomenon such as ‘pop-in’ behaviour due to electrostatic forces caused by polarised micro-particles was also detectable in the measurements.

- A good correlation between the test results obtained through micro-scale approach-retraction curves and conventional test results was observed.

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6 References

