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Contributions of chemical and mechanical surface properties and temperature effect on the adhesion at the nanoscale

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ABSTRACT

The atomic force microscope (AFM) is a powerful tool to investigate surface properties of model systems at the nanoscale. However, to get semi-quantitative and reproducible data with the AFM, it is necessary to establish a rigorous experimental procedure. In particular, a systematic calibration procedure of AFM measurements is necessary before producing reliable semi-quantitative data. In this paper, we study the contributions of the chemical and mechanical surface properties or the temperature influence on the adhesion energy at a local scale. To reach this objective, two types of model systems were considered. The first one is composed of rigid substrates (silicon wafers or AFM tips covered with gold) which were chemically modified by molecular self-assembling monolayers to display different surface properties (methyl and hydroxyl functional groups). The second one consists of model polymer networks (cross-linked polydimethylsiloxane) of variable mechanical properties. The comparison of the force curves obtained from the two model systems shows that the viscoelastic contributions dominate for the adhesion with polymer substrates, whereas, chemical contributions dominate for the rigid substrates. The temperature effect on the adhesion energy is also reported. Finally, we propose a relation for the adhesion energy at the nanoscale. This relation relates the energy measured during the separation of the contact to the three parameters: the surface properties of the polymer, the energy dissipated within the contact zone and the temperature.

1. Introduction

Advances in nanotechnology and miniaturization of devices have led to the requirement of an increased understanding of the interactions and adhesion phenomena at nanoscale contacts [1]. For example, it is well known that adhesion plays a major role in the tribological behaviour and contact mechanics of many modern nano-devices.

In adhesion science [2–6], it is shown that at a macroscopic scale the adhesion energy G between two bodies in contact is dependent on two parameters: the surface chemical properties through the thermodynamic work of adhesion W_0, and the mechanical properties through a function of dissipation ϕ.

One can express the adhesion energy as [6]:

$$G = W_0(1 + \Phi(v,T)) \quad (1)$$

In which, T is the temperature of the bodies in contact and v is the separation speed. In this paper, we focus on the adhesion phenomenon at a local scale.

In recent years, atomic force microscopy (AFM) has become a powerful tool, sensitive enough, to measure low forces with a high resolution at the nanoscale [7–14]. Information about local adhesion [15–17], friction [18], or surface stiffness [19–21] is readily obtainable. In particular, in a previous study, we have demonstrated the capability of the AFM to deduce semi-quantitative and reproducible force measurements [14]. We also have shown that the AFM is able to separate the chemical and mechanical contributions in the adhesion force measurements.

The scope of this paper is to separate the different contributions (chemical, mechanical and temperature) in the measurements of adhesion force. The final objective is to propose an improved relationship of the adhesion energy taking into account the previous physical parameters at the nanoscale. To achieve such goal, we report, in a first part, an investigation of the contributions of the chemical surface properties in the adhesion force measurements in modifying the chemical properties of gold coated silicon nitride AFM tips (in grafting hydrophobic or hydrophilic molecules). In particular, we point out the advantages of the AFM technique in the semi-

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quantitative determination of the thermodynamic surface properties of the material, such as surface energy and thermodynamic work of adhesion, compared to the contact angle measurement technique. The case of the capillary force contribution for highly hydrophilic surfaces is also discussed. In a second part, we investigate the contributions of the mechanical properties of the bodies in contact in studying cross-linked polydimethylsiloxanes (PDMS) with different Young modulus. In a third part, we study the influence of the temperature on the adhesion between a hydrophobic AFM tip and a model polymer networks.

2. Experimental details

2.1. Adhesion force measurements with the AFM on model systems and chemically modified AFM tips

AFM force curves between the AFM tip and the substrate are recorded, in the air, with a commercial apparatus (Multimode IV with a nanoscope III controller, from Veeco) with a relative humidity higher than 30%. The main feature that is obtained from the force curves is the adhesion force. To get semi-quantitative AFM measurements, a rigorous experimental procedure has been established in a previous paper [22] and is applied for this study.

2.2. Materials

To study the surface chemical and mechanical properties that influence the nanoadhesion between two bodies, two model systems are considered. The first one is made of a rigid substrate on which various chemical end groups are grafted or chemically synthesized, whereas the second one is made of a soft polymer for which the Young modulus is controlled and that exhibits the same chemical end groups at the surface than the previous system.

Silicon wafers (100) were chemically modified to exhibit hydrophilic or hydrophobic surface properties. Hydrophobic surfaces are obtained in grafting methyl (CH_3) group terminated molecules (molecules of hexadecyltrichlorosilane ($C_{16}H_{42}Cl_3Si$)-Aldrich, purity of 98%), whereas hydrophilic surfaces are obtained by chemically treated the substrate with a Piranha solution (70% H_2SO_4 and 30% H_2O_2). Silicon wafers covered with hydroxyl end-group (Si–OH) were obtained with this method and immediately probed with the AFM. Typically, the time between the end step of the functionalisation and the first experiment is 10 min. Characterization of the synthesized surfaces is reported in Refs. [22,23]. It confirms that homogeneous and smooth self-assembling monolayers are obtained.

As a soft material, we use cross-linked PDMS substrates (supplied by ABCR, Karlsruhe-Germany). The PDMS macromolecules are vinyl terminated end chains with narrow polydispersity index (Ip equals to 1.5). PDMS cross-linking is achieved under nitrogen, in a glove box, and in using tetrakis(dimethylsiloxy)silane as a cross-linker and a platinum-based catalyst. All the chemicals were supplied by ABCR (Karlsruhe-Germany). The classification of cross-linked PDMS substrates using in this paper refers to the average mass of the chains between cross-linking (Mc) (For example, 1 k refers to a cross-linked PDMS with Mc equals to 1000 g mol^{-1}) that has been determined by swelling measurements of the PDMS in a toluene solution. Thus, PDMS 0.8 k exhibits the higher Young modulus, whereas 16 k refers to the lowest one. The macroscopic mechanical properties are determined by tensile tests and are reported in Table 1. Dynamical mechanical analysis performed on the different cross-linked PDMS has shown that the Young modulus does not vary in the range of temperatures and for a strain frequency of 10 Hz used in this study. In other words, it means that the PDMS network is in the rubbery state in the range of studied temperatures and at the AFM scan frequency.

Table 1
Mechanical properties of the cross-linked PDMS.

PDMS	Chain mass after cross-linking (g mol^{-1})	Elasticity domain (%) ±20%	Deformation at break (%) ±20%	Young modulus (MPa)
0.8 k	800	40	196	2.24 ± 0.3
8.5 k	8500	46	210	0.74 ± 0.1
16 k	16,000	47	250	0.35 ± 0.08

PDMS: polydimethylsiloxane.

To modify the chemical properties of the AFM silicon tip, we use the experimental protocol described in Refs. [24,25]. To summarize, the tip is immersed for 24 h in 1 mM solution of (3-mercapto-propyl) triethoxysilane (MPS) in toluene. Then, 10 nm of gold layer is evaporated on the tip grafted with MPS (ABCR, 99% of purity). The silicon nitride AFM tip was coated with gold under vacuum and in using an Edwards 306 evaporator. In this protocol, MPS replaces the usual chromium or titanium layer used as a linker layer for gold.

The interest of such protocol is that the roughness of the tip is not affected by the deposition of a chromium or titanium layer as a linker of the gold layer. Moreover, the diffusion of the gold in this previous layer is also avoided. After deposition of the gold layer, the tip is cleaned for 30 min in UV/Ozone and immediately immersed for grafting in a 1 mM solution of alkanethiol in ethanol for 18 h. Hydrophobic tips are prepared by grafting 1-hexadecanethiol molecules ($CH_3C_{15}H_{30}SH$, Fluka Chemika, purity of 95%), whereas hydrophilic tips are prepared by grafting 11-mercapto-1-undecanol molecules ($HOC_{11}H_{32}SH$ — Aldrich, purity of 97%). Finally, the tip is rinsed with ethanol and dried under dynamic vacuum for 1 h. Then, the tip is immediately used to do force curve measurements.

3. Results and discussion

3.1. Investigation of the chemical surface properties in nanoadhesion

The nanoadhesion between two perfectly smooth rigid bodies (i.e. rigid contacts and no dissipation energy) is only due to the surface chemical property interactions between each surface into contact. These interactions are quantified in doing AFM force curve measurements between the chemically modified tips and the chemically modified silicon surfaces. Fig. 1 shows two force curves measured in air, and corresponding respectively to a hydrophobic (CH_3 grafting groups) tip/hydrophobic surface (CH_3 grafting groups) interactions, and to a hydrophilic (OH grafting groups) tip/hydrophilic surface (OH grafting groups) interactions.

One can notice that the absolute value of the slope in the contact zone (when the tip is in contact with the substrate) is equal to unity. That means that no indentation of the graftings by the AFM tip occurs. Consequently, the adhesion force (related to the adhesion energy) depends significantly on the surface chemistry of the two rigid bodies in contact. Indeed, the adhesion force increases with the increase of the hydrophilicity of the bodies in contact.

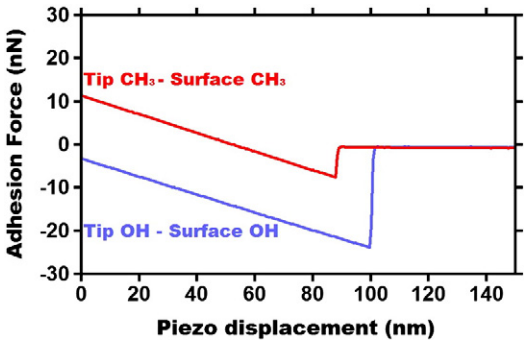

Fig. 1. Force distance curves in air, for n a) hydrophobic/hydrophobic contact b) and hydrophilic/hydrophilic contact.