On the use of SPM to probe the interplay between polymer surface chemistry and polymer surface mechanics

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Abstract. Adhesive properties of a polymer surface results from the complex contribution of surface chemistry and activation of sliding and dissipating mechanisms within the polymer surface layer. The purpose of this study is to dissociate the different contributions (chemical and mechanical) included in an AFM force-distance curve in order to establish relationships between the surface viscoelastic properties of the polymer, the surface chemistry of functionalized polymer surfaces and the adhesive forces, as determined by C-AFM experiments. Indeed we are interested in the measurements of local attractive or adhesive forces in AFM contact mode, of controlled chemical and mechanical model substrates. In order to investigate the interplay between mechanical or viscoelastic mechanisms and surface chemistry during the tip-polymer contact, we achieved force measurements on model PDMS polymer networks, whose surfaces are chemically controlled with the same functional groups as before (silicon substrates). On the basis of AFM nano-indentation experiments, surface Young moduli have been determined. The results show that the viscoelastic contribution is dominating in the adhesion force measurement. We propose an original model, which express the local adhesion force to the energy dissipated within the contact and the surface properties of the material (thermodynamic work of adhesion). Moreover we show that the dissipation function is related to \( M_c \), the mass between crosslinks of the network.

1. Introduction
Precise analysis of adhesive and mechanical properties, and in particular, of model polymer surfaces can be achieved with a nanometer probe. The purpose of this study is to dissociate the different contributions (chemical and mechanical) included in an AFM force-distance curve in order to establish relationships between interfacial tip-polymer interactions and surface viscoelastic properties of the polymer. Indeed we are interested in the measurements of local attractive or adhesive forces in AFM contact mode, of model substrates, both on the chemical and mechanical point of view. These are performed with a silicon nitride tip (\( \text{Si}_3\text{N}_4 \)), at ambient temperature, in the air. Considering that the main technical uncertainties have been listed and minimized, surface force measurements are, in a first step, performed on chemically modified silicon substrates (grafted with hydroxyl, amine, methyl and...
ester functional groups). In order to investigate the effects of mechanical or viscoelastic contributions, we achieved force measurements on model polymer networks, whose surfaces are chemically controlled with the same functional groups as before (silicon substrates). Young modulus have been determined on the basis of nanoindentation experiments. The beginning of the loading regime is only considered as hertz theory could then be applied. The results show that the viscoelastic contribution is dominating in the adhesion force measurement. At the end of this study, we propose new relationships, which express the local adhesion force to the dissipation energy in the tip-polymer contact and the surface properties of the material (thermodynamic work of adhesion). Moreover we show that the dissipation function is related to $\text{Mc}$, the mass between crosslinks of the network.

2. Experimental

Si(100) silicon wafers (supplied by MAT TECHNOLOGY France) polished on one side were used as substrate for SAM film grafting. In this paper, “as received silicon (Si as received)” refers to a silicon wafer previously cleaned with ethanol in an ultrasonic bath. That means that a contaminated layer still remains on the surface. Four organosilane grafts (supplied by ABCR Karlsruhe-Germany) were used for the elaboration of homogeneous model surfaces on the substrate. Two hydrophobic model surfaces were prepared by using hexadecyltrichlorosilane (C$_{16}$H$_{42}$O$_3$Si or Si CH$_3$) and 1H,1H,2H,2H-perfluorodecylmethyldichlorosilane (C$_{11}$H$_7$Cl$_2$F$_{17}$Si or Si CF$_3$) and two hydrophilic model surfaces by using (6-aminohexyl) –aminopropyl trimethoxy silane (C$_{12}$H$_{30}$N$_2$O$_3$Si or Si NH$_2$) and 2(carbomethoxy) ethyltrichlorosilane (C$_3$H$_7$Cl$_3$O$_2$Si or Si ester). All other chemicals used in chemical handling (cleaning, synthesis) were of reagent grade or better (supplied by Aldrich).

2.1. Preparation of oxidized silica surface. Before coating, the substrates must be chemically modified in order to get a hydrophilic surface (SiO$_2$). The silicon surface is, first, cleaned with ethanol and dried with nitrogen before oxidation. Then, oxidized surfaces are obtained after cleaning the substrate in a warm Piranha (60°C) solution (3:7 v/v 30% H$_2$O$_2$ and H$_2$SO$_4$ mixture) for about 30 minutes in order to keep a smooth surface, and then, thoroughly rinsed with deionized and twice distilled water. Just before being grafted with organosilane the wafers are dried with nitrogen. This treatment produces a high hydroxyl group density on the surface (SiOH groups), to which functional silanes will adsorb upon hydrolysis [1]. Silicon wafers covered with hydroxyl end-groups (Si OH) were synthesized with this method and immediately probed in order to avoid contamination of the surface by the environment due to the high reactivity of SiOH groups.

2.2. Functionalized SAMs Preparation. Three different techniques are frequently used to obtain SAMs: Langmuir-Blodgett techniques, involving an air-water interface to transfer the assembled film to a solid substrate, solution adsorption of film molecules onto the substrate, and vapour–phase molecular self-assembling technique [2], which uses vapour deposition of the film onto the substrate. Our functionalized SAMs were prepared with the last technique slightly improved in the laboratory [1]. The lack of solvent prevents the SAMs of a possible incorporation of small solvent molecules contamination and defects. Moreover, a previous study [3] showed that the molecular films prepared with this method, are more homogeneous. The silicon wafers are placed above a previously de-aired solution of 100µl of organosilane - 3ml of paraffin mixture. The vapour-phase deposition of the molecular film on the substrate is performed in a vacuum chamber (50 min at 5×10$^{-3}$ Torr) at room temperature.

2.3. Cross-linking and Functionalization of PDMS. PDMS networks as well as their mechanical properties are described in ref.[4]. The PDMS denomination (PDMS 1.5k…53k) refers to the chain mass of PDMS (determined by GPC) before crosslinking. Then, PDMS 1.5k is the hardest substrate whereas, 53k refers to the softest one. PDMS functionalization was done using the vapour deposition technique after that the PDMS substrate was treated by water plasma.
2.4. Characterization of the SAMs. AFM topographic images, XPS analysis, ellipsometric and contact angle with water droplet measurements were performed on the SAMs and showed that we have obtained homogeneous, well packed, organized and stable grafting both on the silicon wafers and PDMS.

3. Results and Discussion

3.1. Force curve measurements and AFM calibration have been fully described in ref.4. In addition, checking regularly and randomly the adhesion force on a reference silicon wafer verifies contamination of the tip during the measurements. When the tip is contaminated, a new tip is used and characterized. In that way, we can select tips with about the same radius and the same spring constant in order to compare the experimental values. We mention that tip contamination occurs a few in comparison of the great number of realized DD curves. Finally, the reported results are an average of about 100 DD curves for each substrate.

3.2. The tip-sample interaction force was first measured on chemically modified SAMs obtained on undeformable substrates (silicon wafers) and was compared with that for as received silicon wafer. Figure 1 shows that AFM measurements in our conditions are sensitive and significant to a chemical modification of the layers. When jump-off (or jump-in) contact occurs, we measure the corresponding pull-off deflection (or pull-in). Pull-off deflection values (Dpull-off) increase in the following order: Dpull-off,SiCF3 < Dpull-off,SiCH3 < Dpull-off,asreceived < Dpull-off,Siester < Dpull-off,SiNH2 < Dpull-off,SiOH.

Knowing the pull-off deflection one can easily deduce the adhesion force, if the cantilever spring constant k is known (Fadh = k Dpull-off). k has been determined in ref.4. The pull-off deflection and thus the adhesion force value increases with the hydrophilicity of the surface. The measured adhesion force depends strongly on the tip-sample contact area e.g. on the tip radius in the case of undeformable substrates. Sugawara and al.[5] suggested that the adhesion force is proportional to the tip radius. From the DMT theory [6], which established a relationship between the adhesion force (F) and the thermodynamic work of adhesion (W₀) (F = 2πRW₀ (R tip radius)), we can deduce W₀ from experimental adhesion forces. Figure 2 shows that normalized W₀ decreases linearly with the surface energy deduced from classical wettability measurements. This linear correlation is obtained after correction from capillary forces observed on SiNH2 and SiOH wafers. In air a capillary bridge is formed for SiNH2 and SiOH and the pull-off mechanism is different from the other surfaces. The capillary force...
is expressed as follow: \( F_{\text{cap}} = 2\pi R \gamma_w \left( \cos \theta_{w,\text{tip}} + \cos \theta_{w,\text{wafer}} \right) \) where \( \gamma_w \) is the surface tension of water, \( R \) the tip radius and \( \theta \) the contact angle between water and the tip or water and the wafer.

![Figure 2: Thermodynamic work of adhesion deduced from the DMT theory](image)

3.3. A comparison between the DD curves obtained on a silicon substrate and on a PDMS substrate clearly shows the significant contribution of the mechanical properties of the polymer (figure 3). First compared to silicon wafer, in the tip-polymer separation process, the jump-off contact occurs over a large piezo displacement scale and could correspond to a progressive dewetting of the tip by polymer chains during retracting. Secondly, the jump-off amplitude is higher than for silicon wafer. Finally, the loading and unloading slope in the DD representation is much lower than unity in the case of soft polymer systems. Considering all these specificities, we succeed in determining Young moduli from force-indentation curves deduced from DD curves (see ref.5). Results confirm a good control of the network synthesis.

![Figure 3: Comparison between a DD curve obtained on a silicon substrate (top) and a PDMS substrate (bottom). Slope \( S = 1 \) for a rigid material and \( S < 1 \) for a soft material.](image)

We consider now PDMS of different Young modulus grafted with identical molecules than for the SAMs of silicon wafers (CH\(_3\) and NH\(_2\) SAMs). The following ratios \( \frac{F_{\text{adh},\text{PDMS}}}{F_{\text{adh},\text{SiX}}} \) (where \( F_{\text{adh},\text{PDMS}} \) and \( F_{\text{adh},\text{SiX}} \) are the adhesion forces on PDMS and silicon, respectively) can be used to compare the adhesion strengths.
and $F_{adh}$ represents the adhesion force measured on respectively PDMS and silicon substrates and $X$ represents the functionality of the grafting) were calculated for all the grafting and PDMS substrates and compared. It appears that for a given PDMS substrate (for example, 1,5k), the ratios are independent of the surface chemistry, whereas for a given grafting, the ratios are dependant on the mechanical properties of the substrate, with the same values for all the grafts. Thus, for a given substrate, $F_{adh_{PDMSX}} = F_{adh_{SiX}} \times k$ (k is a constant). However, for an undeformable substrate, the DMT theory [7] gives: $F_{adh_{SiX}} = 2\pi R W_0$ (where $R$ is the tip radius and $W_0$ is the thermodynamic work of adhesion). Then, $F_{adh_{PDMSX}} = 2\pi R W_0 \times k$ and when introducing a dimensional constant ($k' = (2\pi R)^{-1}$) the relationship becomes: $F_{adh_{PDMSX}} = W_0 \times k \times 2\pi R \times k'$ or $G_{adh_{PDMSX}} = W_0 \times \phi(v,T)$ (where $G$ is the separation energy and $\phi(v,T)$ is a viscoelastic dissipation function dependant on temperature $T$ and separation rate $v$). This relationship clearly expresses the mechanical contribution from the chemical one in a force curve measurement with AFM. $\phi(v,T)$ is determined for each substrate for a given rate and a given temperature and is independent of the surface chemistry.

| PDMS | $\Phi(v=10Hz,T=293K)$ |
|------|------------------------|
| 1,5k | 1.1                    |
| 11k  | 1.6                    |
| 53k  | 2.2                    |

Table 1: Average viscoelastic dissipation function for PDMS networks

4. Conclusions

The studied model systems allowed us to express the mechanical and chemical surface contributions in a force curve measurement and to establish a relationship, which is quite similar to the relationship of Gent and Schultz [6] at the nanoscale. From then on, a new relationship is proposed to determine thermodynamic surface properties of viscoelastic materials.

References

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