Nano-friction of polystyrene: the role of the surface chemistry

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Abstract. The purpose of this study is to analyse the influence of the chemical contribution on the nano-friction of polystyrene. The role of interfacial interactions is analysed by comparing friction between the polymer and hydrophobic AFM tip (methyl-terminated grafted layer) and hydrophilic tip (hydroxyl-terminated tip) as a function of sliding velocity and normal force. Nano-friction experiments are achieved by using atomic force microscopy (AFM) in torsion mode. Amorphous atactic polystyrene films are prepared by spin coating a solution onto a smooth and rigid substrate (silicon wafer). Two amorphous atactic polystyrene, varying by their different molecular weights are used. Experimental results show that the friction coefficients measured with hydroxylated tip are always larger than those obtained with non-treated tip (intermediate value) and hydrophobic tip (lower friction), indicating a relationship between nano-friction and interfacial interactions. The dependence of frictional force on velocity is consequent, with a great increase of friction with speed in the case of the hydroxylated tip. A higher friction is obtained for the higher molecular weight polystyrene in contact with hydroxylated tips. However, differences between both polymers become negligible in the case of non-treated and hydrophobic tips.

1. Introduction
Atomic force microscopy (AFM) is a powerful tool to investigate nano-friction behavior of polymer surfaces down to the macro-molecular scale. The role of interfacial interactions in friction of amorphous polymers at the molecular scale is not well understood. Self-assembled monolayers (SAMs) formed by adsorption of organic molecules on solid surface, can be used to modify the surface chemistry of AFM tips. This approach allows to control the surface chemistry and thus the surface energy without varying the surface roughness, contact geometry and mechanical properties.

The objectives of the current study are to specify the role of interface in nanoscale friction of amorphous polymers (polystyrenes). The role of interface chemistry is then investigated by comparing nano-friction of polystyrene against hydrophobic AFM tips (methyl-terminated), hydrophilic tips (hydroxyl-terminated) and non-treated tips as a function of sliding velocity and normal force. The influence of polystyrene molecular weight is also analysed.

2. Materials and techniques
Two amorphous atactic polystyrenes (referred to as PS A and PS B), purchased from Sigma-Aldrich were used. Polystyrene films are prepared by spin coating (1000 rpm) a solution in toluene onto cleaned silicon (100) wafers. The average molecular weight Mw of polystyrenes is equal to 190,000 g/mol for PS A and 240,000 g/mol for PS B (polydispersity index equal to 2 for both polymers). The cast films are dried in oven at 120°C above PS glass transition temperature for 30 min to remove
residual toluene. Tapping mode AFM images in ambient conditions show homogenous film surfaces with a root mean square (rms) lower than 1 nm.

A Nanoscope III (Digital instruments) scanning force microscope with commercial silicon nitride (Si₃N₄) tips on triangular cantilevers was used to characterize the nano-adhesion and nano-friction of polystyrene films in ambient conditions. Nano-adhesion is quantified from force curves (obtained for a deflection set point equal to zero). The maximum cantilever deflection measured during the tip/surface separation is directly proportional to the adhesion force. Nano-friction is measured in contact mode, and the mean values of the friction force were extracted from friction loops, the trace minus retrace value (TMR) being proportional to the friction force. AFM probe tip surfaces are chemically treated to obtain hydrophilic and hydrophobic tips with respectively hydroxyl-terminated and methyl-terminated surfaces.

Hydrophilic tips preparation: Si₃N₄ tips are rinsed and sonicated in acetone for 15 min, washed with deionized water, and then oxidized in piranha solution (H₂SO₄/H₂O₂, 70:30 v/v) at 60 °C for 30 min (sulfuric acid and hydrogen peroxide are powerful oxidizing agents). At the end of the immersion time, tips were rinsed with deionized water and dried under a stream of nitrogen. The tips treated in this way are rich in hydroxyl groups at the top of the surface and are suitable for silanization. (Caution: The piranha solution is a strong oxidant and reacts violently with organic substances, it should be handled with extreme care).

Hydrophobic tips preparation: After the cleaning and the activation step, tips are immersed into a solution of 0.1 vol% hexadecyltrichlorosilane (HTS) in carbon tetrachloride (CCL₄) for 8h at room temperature. The HTS molecule was supplied by ABCR. Following the methyl-terminated SAM formation, the tips are rinsed and sonicated in CCL₄ solution to remove any excess of physisorbed silanes, rinsed with deionized water and dried under a nitrogen flow.

Non-treated tips are also used.

3. Results and discussion

Nano-adhesion between AFM tips and polystyrene surfaces has been firstly quantified from force curves experiments. Table 1 presents the maximum deflection and the corresponding adhesion force measured for both polystyrene and the different AFM tips.

| Tip       | Δ Z(deflection) (nm) | F_adhesion (nN) |
|-----------|----------------------|-----------------|
|           | PS B | PS A | PS B | PS A |
| Si₃N₄-CH₃ |      |      | 90 (±5) | 80 (±5) | 15 (±1) | 14 (±1) |
| Si₃N₄-O₂  | 130 (±10) | 90 (±10) | 22 (±2) | 15 (±2) |
| Si₃N₄-OH  | 550 (±20) | 460 (±20) | 94 (±5) | 78 (±5) |

Table 1: Deflection and adhesion force between polystyrene surfaces and AFM tips

Results indicate a higher adhesion for the hydroxylated tip. The lower adhesion is measured for hydrophobic tip. A good correlation between surface energy and nano-adhesion levels is then observed. Moreover, the higher molecular weight polystyrene exhibits a greater adhesion, however, the difference between both polymers is more significant in the case of hydroxylated tips compared to the other tips, that means that a sufficient adhesion level is needed to induce difference between both polymers.
Nano-friction experiments have been carried for different experimental conditions. The influence of normal load (more exactly the corresponding deflection set point value in volts) and sliding speed (equal to the tip velocity, obtained by varying the scan frequency) are analysed. The dependence of frictional force upon load is firstly studied with a constant sliding speed of 0.2 µm s⁻¹. Figure 1 illustrates the variation of the friction force versus the applied normal force.

Figure 1: Friction force versus applied load at 25°C for a sliding speed equal to 0.2 µm s⁻¹

The friction force is proportional to the Trace Minus Retrace value, TMR, in Volts, equal to the difference between lateral forces scanning left-to-right and right-to-left. Figure 1 shows that the friction force increases with the applied normal load roughly in a linear manner, whatever the tip and polystyrene. This linear increase of friction force proves that the friction coefficient is independent on the applied normal force. Figure 1 also indicates that the friction forces (TMR values) are higher for the hydrophilic tips. This higher friction is induced by the greater adhesion level between polystyrene surfaces and hydrophilic tips.

The friction measured for hydrophilic tip is also in good correlation with macro-friction results, which have shown a higher friction coefficient for a polystyrene-hydrophilic wafer system compared to a polystyrene-hydrophobic wafer couple [1, 2].

Elsewhere, quite identical values are obtained for PS A and PS B for nano-friction against hydrophobic and non-treated tips. However, a greater friction force is observed for PS B compared to PS A, in the case of hydrophilic tip.

The dependence of frictional force on velocity is illustrated in figure 2. A great increase is observed for hydrophilic tips. However, the evolution of friction with speed is not significant in the case of hydrophobic and non-treated tips.
Figure 2: Frictional force versus sliding speed (recorded for a normal load equal to 2nN)

The increase of friction with speed is well known for polymer materials and can be explained by viscoelastic dissipation phenomena. Energy is indeed dissipated by the movement, elongation, disentanglement (and perhaps break) of polystyrene chains during the sliding of the AFM tip onto the polymer surface, and a higher sliding speed implies then more dissipation losses, due to more difficult movements (less time to relax).

Experimental results indicates that the friction speed has a great influence on friction force in the case of hydrophilic tips, contrary to hydrophobic and non-treated tip. These difference in speed dependence can be explained by the stronger interfacial interactions between hydrophilic tip and polystyrene surface. These stronger interactions are then able to induce more chains deformation and consequently dissipation, involving a detectable speed dependence, characteristic of a viscoelastic behaviour. The presence of a water layer onto hydrophilic tip surface can also play a role, with the possibility of acid-base interactions between polystyrene and water molecules, but also the formation of capillary bridges.

Figure 2 also shows a higher friction for PS B compared to PS A, in the case of hydrophilic tips. This result is in good agreement with nano-adhesion behavior, which indicates a greater adhesion level for PS B, detectable in the case of hydrophilic tips. For hydrophobic and non-treated tips, quite similar friction values are obtained for both polystyrenes. This result was not observed at macro-scale: friction coefficients of PS A and B were similar, whatever the nature of the substrate (hydrophobic or hydrophilic wafers) [1, 2].

Longer chains of PS B are able to develop a greater adsorption on the AFM tip. More strong interactions can then be formed between PS B and of hydrophilic tip, compared to PS A. These greater interactions, associated to more dissipative chains movements (extraction of longer chains requires more energy) are able to explain the higher nano-friction and nano-adhesion of PS B [3-5]. Greater adsorption ability of PSB on hydrophilic AFM tip is illustrated on figure 3.
In the case of PS B, the high surface energy of hydrophilic tips allows the development of stronger interactions. These stronger interactions will be more numerous in the case of PSB, its longer chains inducing a greater molecular adsorption on the tip surface. These interactions will activate dissipation mechanisms, both effects leading to a higher friction force compared to PSA.

4. Conclusion

The objective of this work was to analyse the role of interface in nano-friction of polystyrene. Experimental results have shown that the change of the chemical surface nature by using AFM tip surfaces terminated by OH or CH3 end groups profoundly affected the nano-friction behavior. The friction values of hydrophilic tips are indeed always larger than those obtained with hydrophobic tips. A logical relationship between friction and interactions forces is then observed, with a good correlation with nano-adhesion results. Elsewhere, the friction coefficient is not significantly influenced by the applied normal load. The dependence of frictional force on velocity is consequent, with a great increase of friction with speed in the case of the hydroxylated tip. The evolution is lower in the case of non-treated and hydrophobic tips. A higher friction is also obtained for the higher molecular weight polystyrene in contact with hydroxylated tips. However, differences between both polymers become negligible in the case of non-treated and hydrophobic tips. Explanations based on the role of adhesion interfacial interactions coupled with viscoelastic dissipation are proposed. The role of interfacial interaction is then complex and such model tips allow to better understand the molecular mechanisms responsible of friction. It could be interesting to clarify the influence of polymer viscoelastic properties on friction by performing friction tests at different temperatures. Multi-scale approaches appear therefore to be necessary to better understand frictional behaviour. Polymer response can indeed be greatly affect by the contact size.

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