Nano-scale friction of polystyrene in air and in vacuum

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ABSTRACT

Using atomic force microscopy (AFM), we measured friction between an AFM tip and a polystyrene surface at 25 °C, as a function of the sliding velocity and the applied normal load, both in air and under vacuum conditions. The objective was to analyze the influence of humidity on the frictional behavior of polystyrene. Our experimental results as a function of sliding velocity revealed a logarithmic increase of the friction force in air whereas a logarithmic decrease of this force is found in vacuum. Our comparative results unveil that two different dissipation mechanisms are dominating the frictional behavior of polystyrene in air and in vacuum. We propose a tentative explanation.

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1. Introduction

Atomic force microscopy (AFM) is a versatile tool helping to develop fundamental understanding of interfacial molecular phenomena [1]. AFM can provide information on surface topography, structure, or organization [2–8], and is also able to probe (by indentation experiments) the thermo-mechanical properties of polymer surfaces, strongly linked to the mobility of polymeric chains at these surfaces. Moreover, the phase contrast mode of AFM allows to distinguish differences in viscoelastic response [9]. Local surface properties such as surface modulus or glass transition temperature (T_g) can indeed differ from the corresponding properties in the bulk.

Lateral force microscopy (LFM), also called frictional force microscopy, measures the lateral or friction force between a surface and a sliding AFM tip, on the nanometer scale [10]. LFM can be used in order to get information about molecular mobility at polymer surfaces [11–13], and is often used to quantify nano-friction properties. Scanning probe methods have been indeed applied to the investigation of nano-scale tribology [14–21]. Performing parallel investigations of identical systems on both macro and nano-scales, nano-friction measurements allow a better understanding of macrotribology properties. However, the correlation between macro and nano-scale results may be delicate in some cases, given that contact areas and velocity ranges being different. Nano-friction is usually strongly dependant on adhesion [22], molecular conformation [17] and surface energy [23].

In addition, the advantage of LFM is also to provide a single asperity (tip) in contact with the polymer surface [24], able to simulate what is happening during friction in nanostructures such as microelectromechanical systems (MEMS) [25,26].

At this contact scale, noting that the surface to volume ratio of the tip is quite large, humidity and presence of adsorbed water (specially on the hydrophilic surface of the tip) can have a major influence on nano-friction due to capillary effects [27,28]. Grigg et al. [29] demonstrated that such capillary forces can be several times larger than chemical interactions between a tip and a sample.

Performing AFM experiments in vacuum represents a way to exclude the effect of adsorbed water, i.e. the contribution of capillary forces is eliminated [29–31]. However, it cannot be completely ruled out that polymer surface properties such as chain conformation and mobility are modified in vacuum.

The goal of this work was to compare nano-scale friction of polystyrene (an amorphous glassy polymer, frequently used as model polymer) in air and in vacuum conditions. The first objective was to identify the effect of humidity on nano-friction. Thus, the evolution of the friction force between an AFM tip and the polystyrene surface was analysed as a function of applied normal force and friction speed. Finally, we developed some hypotheses able to explain the experimental results.

2. Materials and methods

Amorphous atactic polystyrene (PS) was purchased from Sigma–Aldrich and films were prepared by spin coating (1000 rpm) 10 wt% polymer solution in toluene onto silicon (100) wafers, which have been washed and sonicated in acetone, rinsed

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thoroughly with bi-distilled and deionized water and subsequently dried under a nitrogen flow. Average molecular weight and polydispersity index have been determined by gel permeation chromatography (Waters 2690 separation module equipped with three gel columns and a waters 410 refractive index detector) and were, respectively, equal to 191 360 and 2. The cast films were allowed to dry in an oven at 120 °C (PS glass transition temperature T_g is equal to 100 °C) for 30 min in order to remove residual solvent, and then cooled at room temperature (no quenching). Tapping mode AFM images in ambient conditions show homogenous film surfaces with a root mean square (rms) roughness lower than 1 nm. The film thickness was approximately 100 μm.

A Nanoscope III (Digital instruments) scanning force microscope and a multifunctional home built AFM developed in Basel [32] with commercial silicon nitride tips on triangular cantilevers were, respectively, used in air (RH = 40%) and in ultra high vacuum (UHV) (10^{-9} mbar, RH = 0%) to characterize the frictional behavior of polystyrene films. The normal and lateral spring constants of the cantilever were estimated by finite elements analysis [Femlab 3.0, Comsol], and were, respectively, equal to 0.17 N m^{-1} and 248 N m^{-1}. It is important to note that measurements in air and in vacuum have been performed by using two different microscopes, with their own technical characteristics (load and velocity ranges).

The friction force is proportional to the TMR value (Trace Minus Retrace in volt), which corresponds to the difference between lateral forces measured in the left-to-right and right-to-left scanning directions. The mean values of the friction force were extracted from friction loops, which show that the lateral force is fairly uniform over the PS surface.

3. Results and discussion

Measurements are performed using a Si_3N_4 probe tip both in vacuum and in ambient conditions. The friction force was measured as a function of applied normal load and sliding velocity. The influence of the normal force on friction is illustrated in Fig. 1, which shows the variation of average friction force versus applied normal forces in air and in vacuum, for a sliding velocity of 0.2 μm s^{-1}. The frictional force increased roughly in a linear manner with applied normal load for both cases. The linear increase of friction force with load followed the linear behavior of Amonton's law, the slope corresponding to the friction coefficient (μ) [33,34]. Interestingly, μ was considerably higher in air ($\mu = 1.25$) than in UHV ($\mu = 0.065$). Moreover, the observed friction force value at zero normal force (zero-load) which can be linked to adhesion forces, was significantly higher in air (close to 13 nN in air compared to about 4.3 nN in UHV).

The dependence of the frictional force on velocity is illustrated in Fig. 2, for an applied normal load about equal to zero. It is important to note that under such conditions friction of the tip does not induce any scratch or damage of the film. This point has been verified by imaging the surface after friction measurements. We observed that in air the friction force increased logarithmically with sliding velocity (see Fig. 2 – top), whereas on the contrary in vacuum the tendency was opposite, the friction force decreased logarithmically with sliding velocity (see Fig. 2 – bottom).

4. Discussion

Results presented in Fig. 1 indicate a higher friction coefficient and also a greater zero-load friction value in air than in vacuum. The higher zero-load friction force proves that there is significant adhesion between tip and polystyrene surface in air. When the tip and the polymer film surfaces are brought into contact in air, the two surfaces will adhere to each other because of Van der Waals interactions (and acid–base interactions between π electrons of polystyrene and polar groups on the surface of the tip) and the
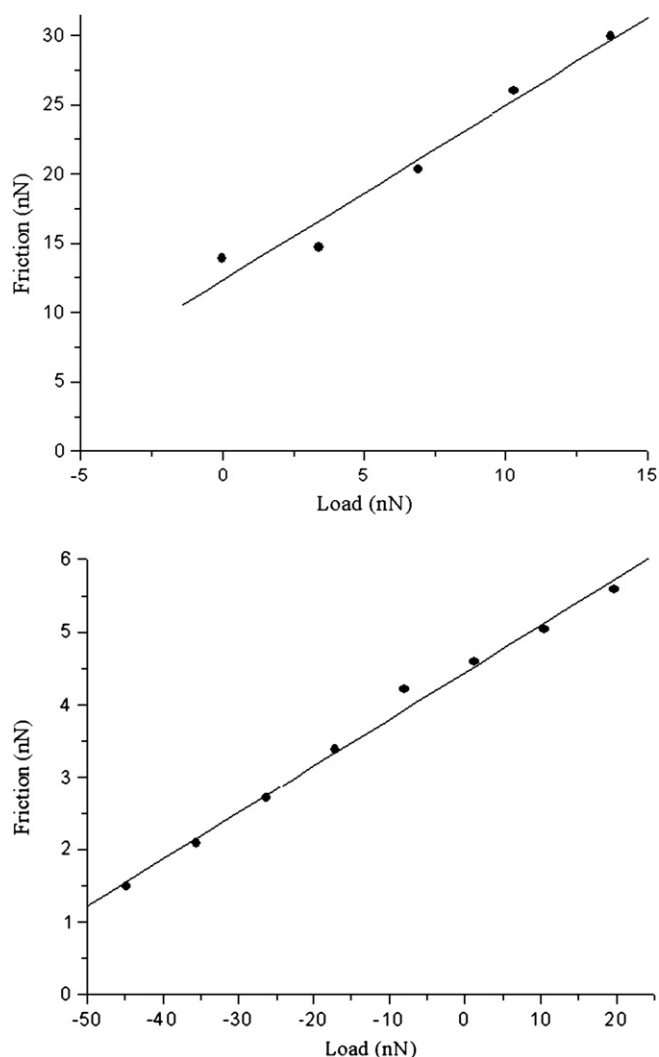

Fig. 1. Friction force versus load recorded at 0.2 μm s^{-1} sliding speed and 25 °C. Top: in air (RH = 40%); bottom: in vacuum.

Laplace pressure of the capillary condensed water at the periphery of the contact zone. Then, the higher friction coefficient in air could be related to a significant adhesion contribution, induced by the presence of a meniscus of adsorbed water molecules (capillary effect).

In vacuum, adhesion was lower, as deduced from the much lower friction force value at zero normal force: in vacuum, the two surfaces adhere only due to the Van der Waals (and acid–base interactions) between the tip and the polystyrene macromolecules at the film surface, without any capillary forces of a water meniscus being possible. The lower level of adhesion might also explain the lower friction coefficient measured in vacuum.

The dependence of friction on sliding velocity is more surprising, with an increase of friction with velocity observed in air, and a corresponding decrease observed in vacuum.

The increase of friction with sliding velocity in air represents a rather common behavior for polymers [35–40]. A similar logarithmic increase of nano-friction with sliding velocity has been also observed for polystyrene films by Sills and Overney [3]. Various phenomenological models based on viscoelastic dissipation and relaxation times have been proposed in the literature. There, viscoelastic dissipation is supposed to occur mainly due to motion, disentanglement (and possibly scission) of chains during sliding of the tip. A higher sliding velocity leads to more dissipative losses
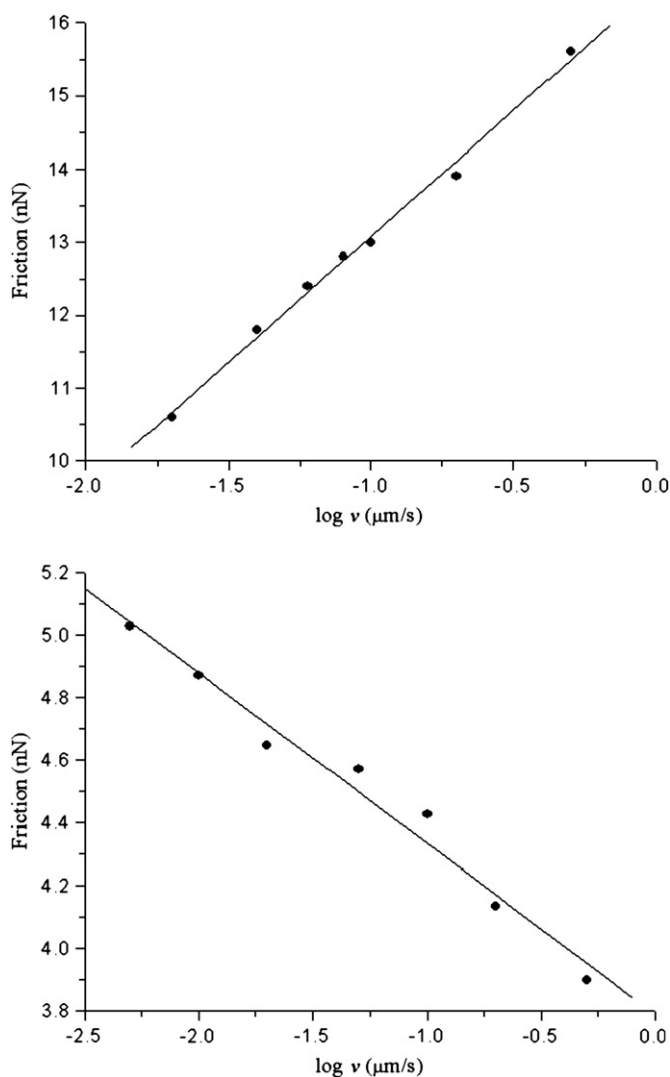
Fig. 2. Friction force versus sliding speed recorded at 2 nN load and 25 °C. Top: in air (RH = 40%); bottom: in vacuum.

caused by faster molecular motions [41,42], with reference to a characteristic relaxation time associated to chain mobility. Another interpretation, which is complementary to this hypothesis, is given by an Eyring-type model [43] of a thermally activated process. In this case, the tip has to overcome a series of energy barriers when sliding across the polymer molecules at the surface. Thermal fluctuation can activate this process, with a "rate of success" being higher for slower sliding velocities [4].

The presence of an adsorbed water layer between the polystyrene surface and the tip, leading to the formation of a water meniscus and stronger interactions between both materials, may induce deformations of the conformations of the polymer chain at the surface and consequently to dissipation. These interactions could be even increased via acid–base bonding between the π electrons of the phenyl group of polystyrene and the tip surface (polar groups present on the tip, e.g. water molecules adsorbed onto the tip) but also induced by the formation of water meniscus bridges.

Furthermore, one may have to consider that the mobility of polymer chains at the surface can differ from the behavior in bulk. Sills and co-workers have investigated by shear-modulated scanning force microscopy the interfacial glass transition of polystyrene films adsorbed onto a solid substrate [44]. Their results indicated the presence of a glass transition temperature (T_g) profile in the

direction normal to the substrate, with a higher T_g (compared to the bulk) in the vicinity of the polystyrene surface.

Kajiyama et al. have found on the contrary, that T_g at the surface of polystyrene films was lower than the bulk T_g [45]. In the case of low molecular weight polystyrene (less than 30 000 g mol^{-1}), the film surface was exhibiting a glass–rubber transition even at room temperature [11].

Forrest and Mattsson have also evidenced a T_g decrease when the thickness of the PS films was reduced [46]. They suggested that the film has a region near the free surface with enhanced mobility due to the release of steric constraints. This mobile surface region has an enhanced rate of conformational transitions. Moreover, McKenna et al. have evidenced two glass transitions in polystyrene/o-terphenyl solution confined in nano-pores: a transition at a lower temperature than the bulk T_g (attributed to a "core" liquid contained within the pores), and a T_g higher than the bulk, due to the existence of an interacting (adsorbed) layer at the pore surface [47]. However, other authors did not find any T_g shift between thin films (thicknesses ranging from 17 nm to 500 nm) and bulk polystyrene [48].

Thus, one may summarize that conflicting results have been published in the literature suggesting that the chain mobility at polymer surfaces may sometimes differ from bulk properties, depending on film thickness, molecular weight, etc.

Furthermore, the presence of water can also modify the mobility of chains at surfaces. Chen and co-workers [49,50] have shown that the decrease of relative humidity can cause a lower mobility of macromolecular chains. Indeed, at a relative humidity of about 40%, water molecules could be able to penetrate the surface of polar polymers leading to an increased mobility of these chains at the surface (plasticizing effect) and additionally imply a weakening of the binding force between macromolecules at the free surface and the interior of the polymer film. Moreover, Reimschuessel et al. [51,52] proved that with a reduction of the moisture content, the glass transition temperature of polymers can increase. However, polystyrene does not exhibit a strong hydrophilic character. Nonetheless, the presence of π electrons is able to induce polar interactions between chains and water molecules.

Results presented in Fig. 2 have also shown that, in vacuum, polystyrene friction decreased logarithmically with sliding velocity. In principle, a decrease of the friction force with sliding velocity could result from a shear-thinning rheological behavior (corresponding to a decrease of viscosity as a function of shear rate). At shear rates larger than 1 s^{-1}, polystyrene is known to exhibit such a behavior as shown in Fig. 3 for the bulk melt state (rheological measurements done at 220 °C with a plate on plate geometry
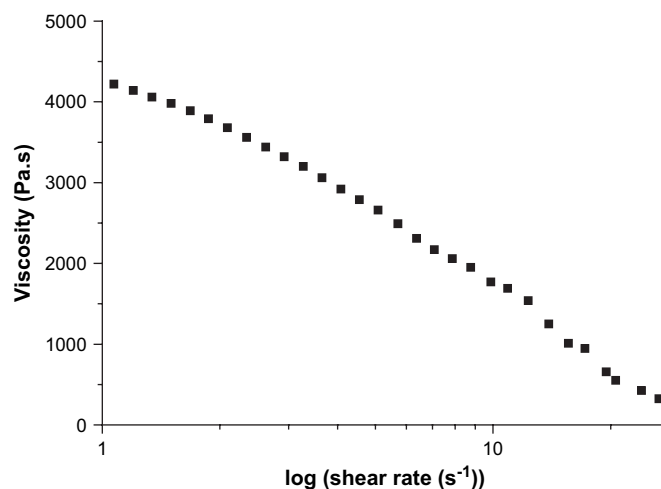

Fig. 3. Viscosity of polystyrene versus shear rate at 220 °C.

MCR500 rheometer). The analogy between friction results in vacuum and rheological measurements could suggest the presence of a liquid-like layer on polystyrene surfaces in vacuum which exhibits a shear-thinning behavior. An increase of sliding velocity could then be able to progressively disentangle some chains, inducing a decrease of friction force. Probably, the rearrangement of the disentangled chains around the probing tip could be a thermally activated process, as recently shown by Riedo et al. [53] who observed a logarithmic decrease of friction with the sliding velocity.

The liquid state of the polymer chains at surfaces could be induced by an increase in thermal energy or sliding velocity and normal load leading to increased heat generation during sliding [54,55]. A temperature increase inside the contact area could allow a softening and a melting of surface chains, which will exhibit a pseudoplastic behaviour during friction.

Polydispersity in chains length may allow for the hypothesis that short chains segregate to the surface in vacuum. However, our polystyrene films were studied at room temperature, i.e. about 75 °C below the bulk T_g, which probably did not allow for such diffusion to the surface during the short experimental time scale.

The presence of a liquid-like layer may also have another origin. The effect of vacuum, i.e. the absence of water, could indeed allow for different chain conformations and chain organizations at the film surface. Unfortunately, the study of properties of polystyrene surfaces in vacuum has received little attention so far, mainly due to the lack of possibilities to perform experiments under such conditions. Sometimes, polystyrene surface properties were studied after a vacuum annealing but then in ambient conditions. However, to the best of our knowledge, in situ experiments, directly performed in UHV, were not described to date. The lack of water may affect chains' mobility and friction at polystyrene surface will then dominated so far not unambiguously identified dissipation process at this interface. Salmeron and co-workers have shown that the friction force (measured by AFM) can vary with sliding velocity in a manner (its increase or decrease) that depends on the chemical nature of the molecules for the interface [56]. The velocity dependence of friction can be quite complex, even for nonpolymeric materials.

Several hypotheses can be proposed for explaining the evolution of friction in vacuum. Open questions are related to a possible shear-thinning behaviour of the polymer surface (decrease of viscosity as a function of shear rate of sliding velocity), or a thermal effect (increase of temperature within the zone of contact) which could lead to a viscosity decrease, and consequently explain the lower friction with speed. Alternatively, the true area of contact could vary with sliding velocity and could so contribute to a change of friction. Many open questions remain also about the role of water in air and the surface mobility of polymer chains at surfaces in vacuum. Our results open up new discussions about the molecular mechanisms involved in friction of polymer. Further in situ analysis in vacuum providing information on surface modulus or T_g could probably give some responses about the origin of the differences in nanotribological behavior of polystyrene in air and in vacuum.

5. Conclusions

Nano-scale friction of polystyrene has been quantified by AFM as a function of the applied normal load and the sliding velocity at 25 °C in air and in vacuum, respectively. Our results show that, as a function of sliding velocity, friction increases logarithmically in air and decreases, also logarithmically, in vacuum. This comparative study demonstrates that the dissipation mechanisms in air and in vacuum are different. Indeed, in air, the increase of the friction force with sliding velocity could be explained by viscoelastic dissipation, thermally activated tip jumps, and also dissipation within the meniscus formed by adsorbed water. However, in vacuum, we

observed that an increase in sliding velocity leads to a decrease of the friction force. This effect could indicate a liquid-like surface layer of polystyrene, exhibiting a shear-thinning behavior. Thus, the role of relative humidity appears to be important, and further experiments, e.g. by varying the relative humidity of the surrounding air or by using hydrophobic AFM tips (to decrease the water meniscus effect), will allow to understand the effect of an adsorbed water film onto friction.

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