Atomic Force Microscopy Friction and Wear Characterization for Composite Materials Coatings

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Atomic force microscopy (AFM) has become established as a significant and versatile tool for investigating local mechanical properties of various materials. In addition, through the AFM tip-sample interaction, it has become possible to study the effects of perturbations and modifications to the surface of samples such as composite materials based on polymers that can ensure a transfer selective in the process of friction, trough formed an antifriction selective layer. The selective layer can get by friction between a surface of steel with a sample of composite material (polytetrafluorethylene (PTFE) with added cooper oxide (Cu_2O) in various greased media) and formed of very thin layer, tribological performed on surface of steel in which predominated Cu. The accurate knowledge of their response to the continuous AFM scanning could help to design new materials with desirable mechanical properties. In this paper, we present results obtained applying a new method to investigate friction and wear properties on the composite material PTFE/Cu_2O. This material is used with high tribological performance at tightening the cylinders of motor vehicles and compressors of petroleum installations.

Keywords: atomic force microscopy, selective transfer, substrate, friction and wear, ripple, topography

Recently there are known materials which in optimal functioning conditions form in the contact zones a thin, superficial copper layer, therefore can function in conditions of selective transfer. In the category of such materials are included also the composites materials based on polymers with added copper oxide (Cu_2O) such as polyamide (PA), polytetrafluorethylene (PTFE) etc.

These materials are used for various friction couples. In the friction zones of these materials special physical-chemical processes take place, which lead to the forming of a thin copper layer; almost pure, with superior properties at minimal friction and wear [1, 2]. This is a request for any friction couple of high efficiency and also a normal process for the self-adjustment phenomena.

In the process of friction of these materials and in the presence of proper lubricants, wear phenomenon manifest itself as a transfer of material from one element of a friction couple to another, this phenomenon being characteristic to the selective transfer process. A selective transfer can be achieved for sure in a friction couple lubricated with glycerin or special lubricant if in the friction zone is even a composite material with added Cu_2O [2-4]. In order to improve the physical-thermal properties, especially of the thermo conductivity and the decrease of friction and wear, it was added to the polymer up to 40% Cu_2O [4]. This copper is different in its structure from the copper obtained through normal electrolytic procedures.

It is well known that the friction resistance between solids is significantly reduced if lubricated. Some experiments, recently performed by Friction Force Microscopy (FFM) addressed the role of interfacial liquid structuring on boundary lubrification [5]. They demonstrated that steel surfaces in contact with composite material (PTFE/Cu_2O) lubricated by glycerin exhibit different dependencies of friction force on load and sliding velocity according to the molecular shape and its specific packing on the substrate. In detail it was found that such effect reduces interfacial friction in nanolubrication.

Despite the potential impact of such observations on nanolubrication technology, lubricants design and fundamental liquids investigations at the nanometer level, very few experiments are still performed in this field by FFM.

Some reasons rely on the difficulty to control tip sample junction during experiments, achieving an efficient trapping of liquid molecules at the typical normal forces of few nanoNewtons.

Realistic molecular dynamic simulations have recently demonstrated that a nanometer-sized asperity can trap liquid molecules up to pressures of about 1 GPa if the liquid is wetting the substrate [6]; otherwise lubricant is squeezed out from contact area and high-friction dry-junction is formed.

In the first case we expect energy dissipation to occur mainly at the boundary layer and within the surrounding medium (due to self-diffusion), while in the second case dissipation should occur only at the dry-junction, the lubricant playing finally a negligible role.

In the following we present FFM measurements for the case of steel surfaces partially wetted by glycerin. We observe that also in the squeezing-out of the lubricant, the surrounding medium seems to have a specific role in the dissipation mechanisms acting between the probe and the substrate.

A fundamental understanding of surface properties of composite materials on nanoscale level should be generated to have a satisfactory knowledge of responses of the structure to friction and wear of the composite materials. The tribological characteristics of these composite materials obtained from added of Cu_2O not been fully investigated. Two aspects can limit the use or efficiency of such composite materials: chemical degradation and/or wear. Chemical degradation starts breaking the long composite material (after one direction) chain into smaller fragments, or causes chain scission and oxidation. Relative motion between parts can cause mechanical damage and generate small debris due to wear.

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The surface of sample from composite material, such as any other material, is not perfectly smooth on a microscopic scale but, rather, has small asperity (roughness) on the surface. Mechanical contact is localized at the asperity. Thus, a relatively low contact pressure for the entire surface can result in very high local pressures relative to any single asperity. Such localized contact pressures can result in adhesion between the asperities of two surfaces in relative motion. After adhesion, subsequent movement can provoke the formation of debris or small fragments. These fragments may react with other chains to form side branches, or react with another chain to form cross-links. The aim of the present paper is to investigate the friction and wear properties on micro/nanoscale, making use of an AFM for composite material PTFE/Cu_2O.

Characterization of friction and wear for the achievement of selective transfer on micro/nanoscale

Among the most important factors to be examined when performing an efficient friction and wear testing is the specimen preparation, the type of motion it is subjected to, type of loading, lubrification and environment control.

Investigation of the fundamental characteristics of friction and wear at the micro-scale is complicated by some factors that act on a nanoscale level, have not yet addresses and are critical to the tribology of macro-systems. Since these forces are sensitive to the environment and surface condition of the specimens, it is quite difficult to determine the forces accurately. Further quantification of friction and wear is not straightforward then amount of wear is often too small to be detected by surface – sensitive instruments. Micro wear measurements have been the object of a rapid development in precise measuring tools following the introduction of AFM [7-10].

The knowledge of friction and wear mechanisms on micro/nanoscale could help to quantify the distribution of material loss during relative motion of surfaces. In fact, weighting the sample before and after the test has been the dominant wear quantification technique. A precision balance typically has a resolution of 10^{-6} of the maximum load, which puts a limit on the minimum load that may be quantified in relation to the total weight of the component. Further, it is important to note that macro wear is 10-1000 times higher that micro-wear on harder material, even though the mean contact pressure in the micro-test is higher than in the macro test. In fundamental research, studies of the temporal evolution of tribological systems starting from the first few stressing cycles are becoming of great interest.

The smallest wear scars often only some tens of micrometers in size require a quantitative technique with a nanometer scale resolution.

The experimental and numerical methods adopted in this paper provide indications on the incidence of different friction and wear-mechanisms. In turn, they should permit a good degree of comparison to be made of the various composite materials employed in industrial applications.

Experimental part

Materials and methods

The samples of composite material PTFE/Cu_2O were made at a cold pressure followed by hardening for 4 h at 370^0C in an oven.

In some experiments, the sample area was formed by two materials with very different hardness coefficients such as a composite material and silicon oxide (SiO_2).

Due to these different hardness coefficients, the responses of the two materials to the stress induced by the repeated passage of AFM probe tip were significantly different. The area of SiO_2 not covered by the composite material was considered as a zero wear reference.

The technique for friction and wear testing consisted of using the AFM probing tip to abrade the surface of interest while simultaneously imaging the area where the composite material was being progressively damaged by the scanning tip. This technique permitted the following friction and wear properties to be observed both qualitatively and, when possible, quantitatively:

-formation of ripples on the surface of the composite material;

-qualitative evolution of the surface before and after the test;

-evolution of friction and wear volume;

-observation of the adhesion effect and subsequent degradation of the probe tip.

The measurements were carried out using an AFM operating in contact mode, with normal force varying in the range 1.0… 12 nN. Images of different areas (256x256 pixels) were acquired using both a silicon nitride tip (pyramidal shape, nominal probe radius 40 nm, cantilever stiffness 0,03 N/m) and a silicon tip (conical shape, nominal probe radius 10 nm, cantilever stiffness 0.24 N/m).

Friction Force Microscopy (FFM) measurements have been performed by means of an AFM operated in air and at room temperature. We have used Si contact probes having a curvature radius less than 10 nm. The substrates have been Si wafers, covered by a $(1\text{-}2)\cdot10^{-3}$nm – thick native oxide layer. The friction force was recovered as a function of applied load and sliding velocity, as reported in detail in [5, 6].

The mechanical contact between the probe tip and the selective layer surface is defined by the following parameters: real area of contact **A**, penetration depth of the probe tip **z**, and yield stress τ, these parameters can be approximated by a model which combines the Hertzian model of elastic contact of a sphere and a flat surface with other models accounting for the adhesion force contribution and possible high applied load causing plastic deformation [11, 12]:

$$A = \pi(3RF/4E_r)^{2/3},\ z = A/2\pi R,\quad \tau = Fn/A, \tag{1}$$

where:

R – is the tip radius of curvature,

E_r – is the reduced Young's modulus of the probe tip and layer.

One relevant aspect in AFM nanoscale study of layer wear is the formation of ripples. These ripples can be considered a consequence of elastic instability waves. They have been observed on a microscopic scale for elastically soft materials such as rubber during sliding on hard surfaces. They have been produced under high load regimes in contact mode, 100 nN, and then observed on high Young modulus composite materials coating [13]. The formation of ripples is commonly considered to be the result of a peeling process operated by the microscope tip on the composite material.

Results and discussions

In order to demonstrate this process on our samples, an area completely covered by selective layer was scanned for 30 cycles at 5 nN with a conical shape probe tip. Figure 1 shows the formation of ripples. Although the first cycle surface is not completely flat, nevertheless, the change of topography is quite evident after 30 cycles.

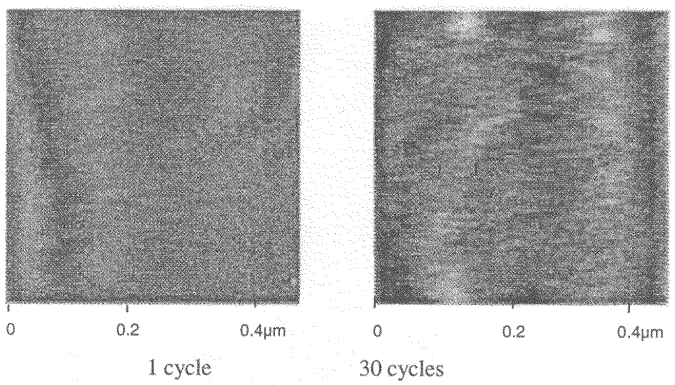

Fig. 1. Evidence of ripples for layer after 30 scanning cycles of probe tip (applied load 5 nN, conical shape tip with nominal radius 10 nm)

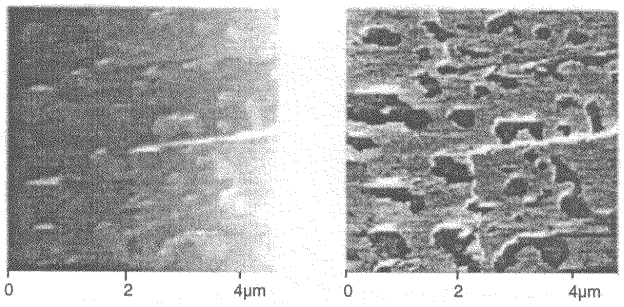

Fig. 2. Surface of SiO_2 covered by composite material ($PTFE/Cu_2O$): a)the image shows the topography; b) the correspondent FMM characterization

The second step of the wear characterization regarded the qualitative analysis of composite material mechanical degradation. To highlight this process and possibly quantify it, a zero wear reference is needed. The zero wear reference was formed by partially covering an area of SiO_2 with the composite material and then abrading that area at low loads and for a limited number of cycles (maximum 10 scanning cycles).Under these experimental conditions, only the selective layer would be exposed to wear due to the significantly higher hardness of SiO_2.

FMM was used when performing the mechanical characterization to highlight the sample area covered by the composite material and to detect variations in the mechanical properties of a surface, such as hardness. FMM allows simultaneous acquisition of both topography and material properties data and it permits local areas where the selective layer covers steel to be distinguished. Figure 2 shows the topography and the correspondent FMM image, and the separation between the area covered by the composite material and SiO_2 substrate is evident. The black domains represent the composite material islands.

Figure 3 represents four different images acquired in different scanning cycles of the same area for selective layer. Image data are square matrices of 256x256 data points containing the height information of the measured surface area. AFM images of the same area acquired in sequence present lateral and rotational shifts. To be able to accurately substrate two consecutive images, they have to be aligned as well as possible in the x-y dimensions before the amount of wear can be calculated. The alignment can be carried out making use of a numerical procedure. The numerical procedure was done in two steps. In the first step, the images had to be laterally adjusted using the cross correlation function. In the second step, they were fitted vertically by multiple linear regressions.

The application of these two steps was justified by the fact that all observed image shifts showed some translation movement and a small degree of rotation [9, 14]. After undergoing the adjustment procedures, the new surface

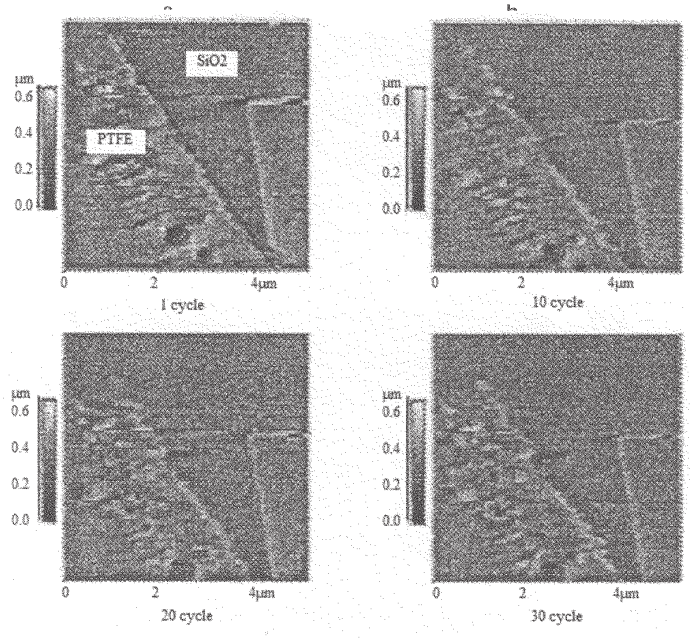

Fig. 3. Four image series for composite material ($PTFE/Cu_2O$)– applied load 1 nN, pyramidal shape tip with nominal radius 40 nm

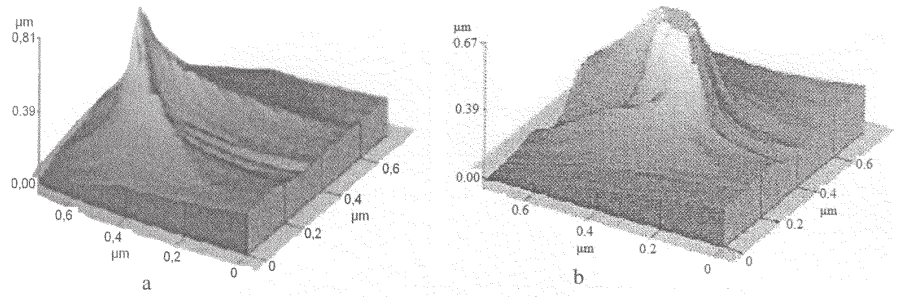

Fig. 4. Images of tip degradation due to adhesion tip wear: a - the convolution of a conical shape probe tip of grating tip before the wear test; b - the same probe tip after the wear test on selective layer

images were compared quantitatively and the degree of change in wear volume was calculated.

Analogously to the procedure normally used in macro scale evaluation, the quantitative analysis of wear mechanisms could carry out using volume change evaluation [15, 16]. The wear volume can be calculated by integrating over the difference of the image data of the total area using the following the expression:

$$\Delta V = V_A - V_B \quad (2)$$

where: V_A and V_B – are two subsequent acquired AFM images after adjustment.

The tribological process was rather complex, involving abrasion, adhesion, plastic deformation and variation of roughness. The behavior of the volume changes, DV, as a function of number of cycles provided complex results that were not easy to interpret.

Generally, it can be expected that the wear volume tends to decrease as the number of stressing cycles increase, due to the plastic deformation of the composite material. Nevertheless, the possible formation of ripples, as described above, should modify the layer surface, working the volume changes due to abrasion difficult to observe.

Resolution limits and errors in volume calculation could be introduced by tip geometry, thermal drift and undetected cantilever twist. The first two types of contributions should not be relevant if a conical shape tip is used and the laboratory is thermally stable. On the contrary, undetected cantilever twist would remain a source of unexpectedly large errors.

Other phenomena like electrical or mechanical noise should not contribute significantly to the error in volume estimation, since volume calculation is a fragmental process and the net contribution should therefore be closed to zero.

The third experiment was conducted to highlight the crucial question of tip wear. The amount of tip wear can be obtained by observing the change of tip geometry before and after the sliding tests. Tip degradation can be generated by two main wear mechanisms, abrasion and adhesion wear mechanisms.

The abrasion wear mechanism on the tip could be activated by the sliding contact on SiO_2, while the adhesion wear mechanism involves the attachment of the composite material to the probe tip. Scanning Electrical Microscopy (SEM) analysis of the tip demonstrated that the wear tests performed at 1 nN did not expose the tip to significant wear mechanisms.

This result confirmed that the experimental conditions were bellow the critical values of applied load and number scanning cycles at which tip wear is observed. Nevertheless, the value for the wear depth/rate could be underestimated, because the nominal applied load (1nN) does not consider the supplementary effect due to adhesive interaction between the AFM tip and composite material exposed to atmospheric conditions. In fact, the adhesive interaction is thought to be stimulated by the presence of relative humidity.

Adhesion force is the sum of the capillary force, due to the Laplace pressure of the water meniscus forming at the tip sample interface and the direct adhesion of the two solids in contact with liquid. The adhesion force is thought to introduce a supplementary force of 0.1…0.2 nN [17, 18]. Generally force-distance curves can help in providing a suitable analysis of tip wearing due to adhesion of the composite material to the AFM tip [19, 20].

In figure 4 is showed the effect of material adhering to tip. The resultant image is the convolution of the probe tip and the grating tip. Probe tip degradation should give a deformed image of the grating tip.

In figure 5 we report the mean friction force as a function of applied load and sliding velocity for the case of dry tip-sample contact.

The friction coefficient between the composite material probe and the SiO_2 substrate covered by a composite material layer is $\mu = 4$ a.u./nN. A logarithmic increase of

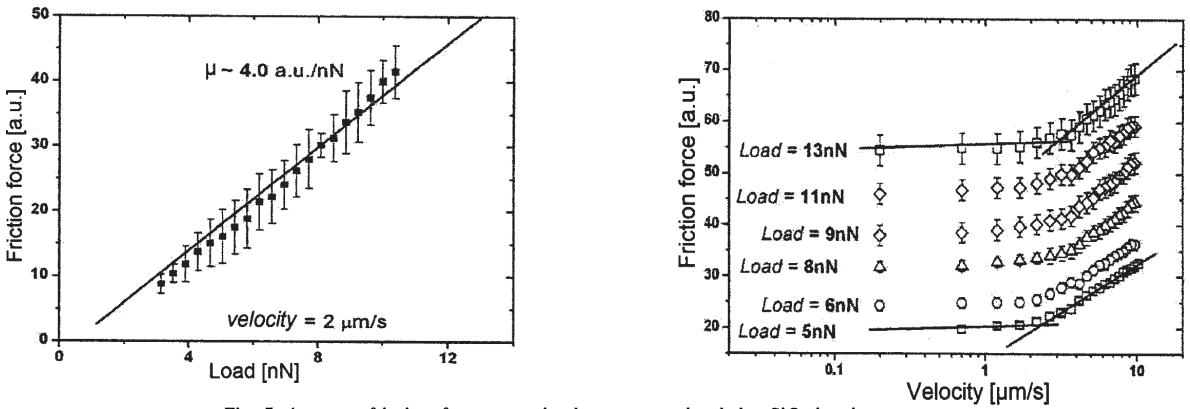

Fig. 5. Average friction force acquired on as-received dry SiO_2 in air: a – average friction force vs load for velocity of 2 m/s; b – average friction force vs velocity for loads of 5-13 nN

friction force is observed above 2 μm/s at the loads in the range 5 -13 nN. We observe that the friction coefficient estimated at the sliding velocity of 2 μm/s is constant for dry, within the achieved experimental resolution (better than 10%). Figure 5 shows that above a critical velocity of about 2-3 μm/s, dissipation rate is not higher for dry jonctions. Moreover the critical velocity values increase monotonically on increasing the normally applied load.

Conclusions

A level nanotribological friction force depended on load and sliding velocity and is performed by FFM measurements with helps of a AFM and for selective layer surfaces on steel substrate.

We have observed that friction force increases linear with load and for small sliding velocities (less than 2 μm/s) the friction coefficient and the dissipation rate are the same for dry and lubricated junctions.

At loads until 12 nN and for small sliding velocities (less than 5μm/s) the friction force increases very logarithmic little and a increased quickly at sliding velocities higher than of 5 μm/s.

Starting from these preliminary results, it has been shown that presented surface analysis method using AFM is a valuable tool to study selective layer friction and wear at micro/nanoscale level. In particular, fundamental local friction and wear phenomena located to a single asperity can be interpreted even of some environmental variables which are not known accurately.

The method could be used as a screening technique when studying the wear (resistance of bio-compatible materials for use in friction couple applications.

The methodology developed made it possible to observe and analyze qualitatively and, when possible, quantitatively some wear properties such as: 1) formation of ripples on the surface of the layers; 2) qualitatively evolution of the surface before and after testing; 3) evolution of wear volume; 4) study of adhesion effects and subsequent degradation of the probe tip. In order to be able to distinguish between the simple wear of the selective layer and the artifacts introduced by AFM tip wear rather than the convolution of sample wear and worm tip, precise alignments between subsequent scanning cycles have been reached as well as possible.

The method described in this paper could be applied in precise environmental conditions such as polymer samples or layer samples, soaked in physiological buffers with determined *p*H.

The experimental and numerical methods adopted in this paper provided good indications on the incidence of some different wear mechanisms. This made it possible to compare with a good degree of precision the wear resistance for different polymers or layers employed in tribological applications.

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