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## **Abstract:**

Due to its superior mechanical properties, nanodiamond holds great potential to improve tribological characteristics of composites. In this study we report on the wear and dry friction of epoxy-ND composites prepared from as-received and aminated ND across the length scale range from macro- to nano. Comparison of macroscale, microscale and nanoscale frictional behavior shows that ND is highly effective in improving the wear resistance and friction coefficients of polymer matrices across the different length scales. Although with both types of ND wear resistance and friction coefficients of epoxy-ND composites was significantly improved, ND-NH<sub>2</sub> outperformed as-received ND, which we account to the formation of a strong interface between ND-NH<sub>2</sub> and the epoxy matrix. This study also shows that agglomerates within epoxy-ND composites containing 25 vol.% ND were able to wear an alumina counter-body, indicating very high hardness and Young's modulus of these agglomerates, that can eventually replace micron sized diamonds currently used in industrial abrasive applications.

*Keywords: Tribology, nanodiamond, epoxy, nanocomposite, friction, wear*

## **1. Introduction**

Wear resistant materials with low friction coefficients are of interest in many applications where surfaces come into contact with each other. Polymers are commonly used to reduce friction between two surfaces, for example as bearings between steel counterparts or as coatings in joint prostheses [1-4]. To improve their tribological performance and produce solid, self-lubricating materials, polymer composites with additives such as graphite, polyether ether ketone (PEEK), bronze and alumina were proven to be effective, even replacing metals, commonly used in high performance wear applications [5,6]. Further improvements in tribological properties are possible when

macroscopic and nanoscopic fillers are combined [7]. Recently it was shown that functionalized nanofillers can improve the wear resistance of thermosetting polymer matrices by up to 800 % [8-10].

Nanodiamond (ND) attracts much attention of the polymer-composite community. Having superior mechanical properties (Young's modulus 1220 GPa, hardness 10 on the Mohs scale), a low friction coefficient [11], excellent thermal conductivity, unique electrical and optical properties [12], biocompatibility [13], ND combines an inert diamond core with a large accessible and reactive surface [14] in a particle of 5nm or less in diameter. It has proven to be an excellent candidate for biomedical [15,16], electrochemical [17], and composite applications [18-20]. Several studies on polymer-ND composites have shown that ND can be used to improve the mechanical properties of polymer matrices [19,21]. To achieve these improvements it is of outmost importance to control NDs surface chemistry depending on the matrix. For example, hydrophobic ND obtained by functionalization with octadecylamine outperformed unmodified ND in a hydrophobic biodegradable poly(L-lactic acid) matrix [18]. Aminated, hydrophilic ND (ND-NH<sub>2</sub>) was used to covalently incorporate ND into an epoxy matrix, resulting in high Young's moduli [22].

Tribological studies on polymer-ND composites are rare, even though it is well known that, in many environments, single and polycrystalline diamond exhibits excellent performance in tribological applications, for example in the form of smooth CVD diamond coatings [23,24]. Lee et al. showed that ND can improve the macroscopic wear resistance of PTFE films [25], while Voznyakovskii et al. reported on improved tribological properties of polyurethane-ND composites [26]. Also, in our previous study, we reported on a stiffened epoxy-ND composite (470 % increased Young's modulus and 300 % increased hardness) with a 40 % decreased friction coefficient due to the addition of 25 vol.% of as-received ND [27]. However, the tribological properties of composites with functionalized ND were not reported. In the present study, tribological measurements on as-received and ND-NH<sub>2</sub>-epoxy composites were performed using macroscale (pin-on-disk), microscale (nanoindentation) and nanoscale (AFM) characterization techniques.

## **2. Materials and Methods**

### **2.1. Materials**

ND powder UD90 (NanoBlox, Inc. USA), with an average particle diameter of 5 nm characterized in [28] was used as-received and after reaction with ethylenediamine (Sigma-Aldrich), resulting in aminated ND (ND-NH<sub>2</sub>). Synthesis and characterization of ND-NH<sub>2</sub> is described elsewhere [22]. The epoxy system Epon828 (diglycidyl ether of bisphenol A; Hexicon, USA) - PACM (bis-p-aminocyclohexyl methane; Air Products, USA) was used in this study. The stoichiometry and resulting properties of this system are well known and are described elsewhere [29]. The predetermined amounts of Epon828, ND/ND-NH<sub>2</sub> were mixed and bath sonicated for 5 minutes in Tetrahydrofuran (Fisher Scientific, 99.9 %,

stabilized). The solutions were stirred in closed vials on a hot plate for 2 days at 50 °C, followed by opening the vials and solvent evaporation for 48 h at 50 °C. For ND concentrations below 12.5 vol.% the composites were cured in 20 mm diameter aluminum molds for 2 h at 80 °C and 2 h at 165 °C following the standard curing procedure for the Epon828-PACM system after adding 28 pph (parts per hundred, i.e. 28 g per 100 g of Epon828) of the curing agent according to stoichiometry of this system [29]. Due to the high viscosity of epoxy-ND samples with contents higher than 7.5 vol.% ND, resulting wet ND/ND-NH<sub>2</sub>-Epon828 pastes were transferred into 5 mm (samples for nanoindentation) and 20 mm (samples for bulk wear tests) diameter hot pressing molds and the curing agent was added. After hand mixing in the mold, the pastes were pressed at a load of 4 tonnes for 2 h at 80 °C and 2 h at 165 °C following the curing procedure. All produced samples were polished for subsequent tribological tests using a Struers RotoPol-22 polishing machine after mounting them into Castolite; LECO, USA. The final polishing step was performed using an alumina polishing solution with an average particle size of 0.05 µm. All samples were cleaned in an ultrasonication bath prior to testing.

## **2.2. Wear and friction measurements**

As previously reported, polymer-ND composites contain ND agglomerates, whose sizes can be divided into the following three groups: 1<sup>st</sup>, > 0.6 µm; 2<sup>nd</sup> -, 0.2-0.5 µm; and 3<sup>rd</sup> -, ~100 nm [30]. Small agglomerates are contained within larger agglomerates and are individually dispersed in the polymer matrix itself. Macroscopic measurements with a pin-on-disk tester give average values for the entire composites, not distinguishing between locally changing properties. Nanoindentation probes properties on the µm scale, for example of single ND-agglomerates. Furthermore, AFM measurements were used to measure properties of ~100 nm ND agglomerates, contained in larger assemblies, with nanometer resolution.

### **2.2.1. Pin-on-disk**

Macroscale tribological properties of test samples were evaluated in open air (35-40% relative humidity) using a pin-on-disk tester (Nanovea tribometer) under a load of 5 N. Sintered alumina and AISI 52100 steel balls with diameters of 3/8" were used as counter-bodies. The testing time for the alumina counter-body was 45 min and it was 480 min for the steel counter-body. Surfaces of the worn composites and the counter-bodies were analyzed using an optical surface profilometer (KLA Tencor, MicroXAM). Line scans were performed using a non-contact MicroXAM profilometer. Friction coefficients were measured continuously at a rotation speed of 10 rpm over a 10 mm track diameter. Reported average friction coefficients were calculated from the data collected in the sliding distance range of 0-6m and 9-14m.

Friction forces were recorded continuously by a data acquisition system. Values of friction coefficients were automatically calculated and tabulated in data tables from which the friction coefficient vs. distance diagrams were extracted. Using the Micro XAM non-

contact profilometer, line scans of wear tracks and counter-bodies were obtained and used to assess the wear damage and calculate surface roughness.

### **2.2.2. Nanoindentation**

Microscale friction coefficients of epoxy-ND composites were measured using a Nanoindenter XP (MTS Corp.) using a 100  $\mu\text{m}$  radius diamond indenter to minimize plastic deformation. Five measurements per sample were performed at a fixed vertical indenter displacement of 300 nm to ensure a close to constant contact area over a sliding distance of 250  $\mu\text{m}$  and an indenter velocity of 10  $\mu\text{m/s}$ . Each sliding test was performed in a single forward pass of the indenter. Friction coefficients were calculated from the lateral and normal forces acting on the indenter. Reported friction coefficients are the average values of 5 measurements.

### **2.2.3. AFM**

Nanoscale properties of unworn composites were characterized using an Agilent PicoPlus 5500 AFM. Prior to imaging, samples were rinsed with methanol and dried in dry nitrogen gas flow. A rectangular silicon cantilever (MikroMasch; San Jose, CA) with a normal stiffness of 0.54 N/m was used for contact mode imaging in ambient air. Topography and friction voltage were recorded for each contact mode scan. The normal cantilever stiffness was calibrated using the Sader method [31], and friction forces were calibrated using the wedge method [32,33].

## **3. Results and Discussion**

### **3.1. Macroscale pin-on-disk**

#### **3.1.1. Wear**

Light micrographs of wear tracks, induced by an alumina counter-body on neat (Figure 1a) and 25 vol.% epoxy-ND (Figure 1b) were captured. Wear tracks of composites containing 7.5 and 12.5 vol.% ND were not observable by light microscopy, indicating a significantly improved bulk wear resistance. At ND concentration of 25 vol.% wear tracks became traceable again using dark field imaging (Figure 1b). Abrasive wear resulting in “smearing” of the composite and extensive perpendicular cracks over inconsistent wear tracks further suggest a “stick-slip” motion of the alumina counter-body on this sample. Also, intact, up to 300  $\mu\text{m}$  ND-epoxy agglomerates found within the wear tracks provide evidence of a significantly higher hardness of the agglomerates compared to the surrounding matrix. Profilometer scans of the alumina counter-body support this hypothesis, showing significant damage after tests on epoxy-ND composites containing 12.5 vol.% ND (Figure 1c). This damage of the counter-body can only be explained if we assume that ND-epoxy agglomerates have a hardness comparable or higher to that of

alumina (up to 20 GPa) [34]. Interestingly, such severe damage of the counter-body has not been observed for composites with higher or lower contents of ND.

To gain more information on the tribological performance of epoxy-ND composites, a softer steel counter-body was used at longer testing distances of 25 m. Topographical images and line scans of the wear tracks (Figure 2a) and steel counter bodies (Figure 2b) on neat epoxy and epoxy-ND composites were produced using optical profilometry. For the neat epoxy sample, wear tracks and debris were observed, while the steel counter-body did not show any signs of damage. At a ND loading of 4 vol.%, steel counter-body and wear track line scans show almost no wear. ND loading of 7.5 vol.% ND further improves the wear resistance of the composites, as topographical images and line scans show almost no removal of material. At the same time the steel counter-body gets damaged, probably cut by ND agglomerates contained within the wear debris building up during testing. This effect becomes more pronounced when further increasing ND loadings to 12.5 vol.%. The damaged steel counter-body introduces deeper grooves into the composite, i.e., up to 3  $\mu\text{m}$  deep. We suspect that ND-agglomerates at ND contents below 25 vol.% get pulled out of the matrix, damaging the counter-bodies. However, at ND concentrations of 25 vol.% the steel counter-body stays almost intact and less wear of the composite is measured. At this high concentration of ND the composites can be thought of as a porous ND-body infiltrated by epoxy [27], explaining the reversed trend in the tribological behavior, observed for both, steel and alumina counter-bodies: The high wear resistance of these composites prevents plowing of the wear tracks, resulting in a smaller contact area and making ND agglomerate pull-out difficult. A previous study of Polytetrafluoroethylene (PTFE)-ND composites reported on the effect of agglomerate size on the wear performance of the composites. Smaller agglomerate size was found to decrease wear rate [35]. We assume that the same effect is taking place in epoxy-ND composites, explaining the better performance of epoxy-ND composites containing 7.5 vol.% ND.

To understand the effect of surface functionalization of ND on the tribological performance of epoxy-ND composites, samples with 2 vol.% of ND-NH<sub>2</sub> were tested. Even at this low concentration of ND-NH<sub>2</sub> the wear resistance of the composites is significantly improved (almost no wear was observed; Figure 2a). At the same time, the steel counter-body shows the most severe damage within this study (Figure 2b), resulting in a rougher wear track (Figure 2a). The strong interface between covalently incorporated ND-NH<sub>2</sub> particles and the epoxy matrix prevents pullout of ND-NH<sub>2</sub>, which can explain the improved wear resistance. At the same time the high hardness of ND causes the severe damage of the steel counter body.

### 3.1.2. Friction

Continuously recorded and averaged macroscale dry friction coefficients calculated from macroscopic pin-on-disk test data in the range of 0-6 and 9-14 m are shown in Figure 3a-c. The stabilization of friction coefficients at longer testing times for neat epoxy and all

epoxy-ND composites suggests plowing of the wear tracks, resulting in an increased surface area. This hypothesis is confirmed by the significant decrease in standard deviations of averaged friction coefficients measured in the range of 9-14 m when compared to the initial ones in the range of 0-6m: larger initial fluctuations in friction coefficients are related to the variation in topography prior to testing. When the test progresses (longer testing distance), the standard deviation of friction coefficients decreases due to the formation of wear tracks (Figures 3b and c). This is confirmed by comparing the surface roughness ( $R_a$ ) prior to testing (Figure 3a, inset): due to the different responses to polishing of the neat epoxy and epoxy-ND composites,  $R_a$  values differ. Therefore friction coefficients prior to plowing cannot be compared. However, after plowing of the wear tracks, smoothing the surface, friction coefficients can be fairly compared (9-14m (Figure 3a)). Friction coefficients decrease from  $0.80 \pm 0.05$  for neat epoxy to  $0.67 \pm 0.03$  for a 4 vol.% ND composite, slightly increasing over the testing distance (Figures 3a and c). Addition of 7.5 vol.% ND to epoxy results in a 4 times lower friction coefficient of  $0.19 \pm 0.02$ , the largest decrease in bulk friction coefficient measured in this study (Figure 3c). In contrast to the other composites, the initial friction coefficient for 7.5 vol.% ND is stable and has a remarkably low value of  $0.1 \pm 0.02$ , increasing at a sliding distance of about 13 m (Figure 3a). The start of abrasive wear at 13 m might result from a weak interface between ND agglomerates and the epoxy matrix, leading to agglomerate pull-out. The friction coefficient of a composite containing 12.5 vol.% ND stabilizes at a value of  $0.60 \pm 0.03$ . A composite with 25 vol.% ND has a friction coefficient of  $0.70 \pm 0.03$ , nearly constant over the entire testing distance, indicating almost no plowing and thus a high wear resistance. The slightly higher friction coefficients for composites containing higher loadings of ND might originate from an uneven composite morphology, where ND agglomerates stick out of the matrix, hindering the counter-body movement. The 25 vol.% ND composite has the highest surface roughness prior to testing (Figure 3a, inset).

Epoxy composites containing ND-NH<sub>2</sub> perform rather differently: The friction coefficient initially increases to  $0.8 \pm 0.1$  and then decreases with sliding distance, stabilizing at a value of  $0.68 \pm 0.05$ . The high initial increase is in agreement with the observed severe damage of the steel counter-body and the higher surface roughness measured prior to testing, originating from the sample response to polishing. We account the improved performance at long testing times to a stronger interface between ND-NH<sub>2</sub> and epoxy, resulting from the covalent incorporation of ND-NH<sub>2</sub> into the epoxy matrix [22], improving the wear resistance of the composite.

### **3.2. Microscale test using nanoindentation**

To gain further insights into the friction behavior at the micrometer scale, nanoindentation sliding tests were performed. Averaged and continuously measured friction coefficients are shown in Figure 4a and b. With as-received ND, averaged microscale friction coefficients are significantly reduced from  $0.30 \pm 0.03$  for neat epoxy to

0.2 ± 0.1 for the 5 vol.% ND composite. Further increases in ND contents to 33 and 50 vol.% result in decreased friction coefficients to 0.13 ± 0.04 and 0.08 ± 0.02 respectively. The low microscopic friction coefficients at high ND contents stand in contrast to the measured macroscopic friction coefficients, the latter increased at ND contents higher than 7.5 vol.%. This is an illustration of the difference between bulk and microscopic properties. The sliding length of the nanoindenter is only 250 μm in comparison to 24 m in macroscale tests. At these small length scales it becomes possible to measure friction coefficients on single ND-agglomerates, where ND concentration within ND-agglomerates is high and constant. Furthermore, variations in the area of contact between macroscopic and microscopic measurements, resulting from the differences in indenter size and displacement, contribute to the observed differences. To further investigate the influence of surface roughness on microscopic friction coefficients, data was recorded continuously and is shown in Figure 4b. According to these measurements surface roughness does not seem to be the major mechanism for reducing friction coefficients of epoxy-ND composites, since differences in surface roughness (fluctuations of friction coefficients) between neat and high concentration ND samples (33 and 50 vol.% ND/ND-NH<sub>2</sub>) are similar, but friction coefficients for epoxy ND composites are reduced by a factor of six. These results further suggest that uniform ND dispersion is essential to optimize composite properties, minimizing surface roughness, and show the potential of ND for tribological applications.

The addition of 5 vol.% aminated ND-NH<sub>2</sub> results in a friction coefficient of 0.15 ± 0.06, being slightly lower than the values measured on composites prepared with as received material. This effect becomes more pronounced at higher ND-NH<sub>2</sub> loadings: a 33 vol.% ND-NH<sub>2</sub> composite shows the lowest measured friction coefficient within this study, 0.06 ± 0.02 (Figure 4a), being ~50% less when compared to the composite produced with 33 vol.% of as received ND (0.13 ± 0.04). This value is close to the one reported for pure carbide-derived (0.2) [36] or diamond-like carbon films (0.05)[37].

### **3.3. Nanoscale friction using AFM**

To understand reinforcing mechanisms of as-received ND and ND-NH<sub>2</sub> on the epoxy matrix, AFM measurements were performed. Friction force and topographical maps on neat epoxy and epoxy-ND/ND-NH<sub>2</sub> composites containing 12.5 vol.% are compared in Figure 5. Constant friction forces and a smooth topography were measured on the neat epoxy sample. Scans performed on single ND-agglomerates within epoxy-ND composites containing 12.5 vol.% ND show inconsistent behavior (notice the areas with higher and lower frictional forces in Figure 5), revealing ND clusters, with diameters of ~100 nm within the epoxy-ND agglomerates. Friction forces are significantly lower than those recorded on the agglomerate matrix material and a sharp change in friction force is observed upon transition from either region (Figure 6a). Thus, it is likely that weak interactions between ND-clusters and the epoxy exist, being supported by topographical scans (Figure 5), showing harder ND clusters sticking out of the sample surface. We

suspect that the ND clusters can easily be pulled out of the epoxy matrix when a counter-body is sliding over the surface. Composites made with ND-NH<sub>2</sub> have a rather different structure: transitions between low and high friction force areas are smoother and have a lower amplitude (Figure 6b). Also, ND-NH<sub>2</sub> clusters have smaller sizes of ~50 nm (Figure 5; 12.5 vol.% ND-NH<sub>2</sub>), and suggest better integration into the epoxy matrix, due to the covalent incorporation of ND-NH<sub>2</sub> [22].

#### **4. Conclusion**

Macroscale, microscale, and nanoscale measurements of the tribological properties of epoxy-ND composites have shown significant differences in the tribological behavior at the different length scales. The macroscale wear resistance of composites containing 4 and 7.5 vol.% ND was significantly improved over neat epoxy, as confirmed by light microscopy and optical profilometer scans of wear tracks and counter-bodies after macroscopic pin-on-disk tests. Average friction coefficients were reduced by a factor 4 due to the addition of 7.5 vol.% ND, where the lowest friction coefficient of  $0.1 \pm 0.02$ , an 8 times decrease, was measured. Also, abrasive wear on epoxy-ND composites containing 25 vol.% ND was observed, while composites containing 12.5 vol.% ND severely damaged the alumina counter-body, indicating the highest hardness values of epoxy-ND agglomerates. Thus, epoxy-ND agglomerates have the potential to replace micron sized diamonds that are currently used in industrial applications for sawing, grinding and polishing. Composites produced with ND-NH<sub>2</sub>, outperformed composites manufactured with non-aminated ND. Epoxy-ND-NH<sub>2</sub> composites containing 33 vol.% ND-NH<sub>2</sub> have a friction coefficient of  $0.08 \pm 0.02$  in nanoindentation sliding tests, the lowest value measured in this study, coming close to values reported for carbide-derived or diamond-like films. AFM scans on epoxy-ND-agglomerates revealed ND clusters of ~100 nm in size having the lowest friction coefficients, explaining the observed decreases in both, macro- and microscale friction coefficients. These scans suggest covalent incorporation of ND-NH<sub>2</sub> particles that might be responsible for the better performance of ND-NH<sub>2</sub>-epoxy composites.

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## 7. Captions

Fig.1: a) Bright field image of wear tracks on a neat epoxy sample. Continuous removal of material can be observed. b) Dark field image of wear tracks on a 25 vol.% ND sample. Intact ND agglomerates within the wear tracks indicate a high resistance against wear. c) 3D-surface scan of an alumina counter-body after a wear test on a 12.5 vol.% ND epoxy composite showing significant damage.

Fig.2: a) 3D-profile and line scans of wear tracks on neat epoxy, epoxy-ND and epoxy-ND-NH<sub>2</sub> composites. b) 3D-profile and line scans of the steel counter bodies after the tests.

Fig.3: a) Development of friction coefficients over a testing distance of 24m. Steel counter bodies were used for these tests. Inset: surface roughness  $R_a$ , measured prior to testing. b) Averaged bulk friction coefficients in the range of 0-6m and c) 9-14m.

Fig.4: a) Averaged microscale friction coefficients. b) Experimental curves (one out of five) measured using a diamond nanoindenter.

Fig.5: Topographical and friction force maps recorded with AFM on neat epoxy and epoxy-ND composites containing 12.5 vol.% ND and ND-NH<sub>2</sub>.

Fig.6: AFM line scans of epoxy-ND composites containing a) 12.5 vol.% ND and b) 12.5 vol.% ND-NH<sub>2</sub>. Composites containing as received ND show sharp transitions in frictional forces. The usage of ND-NH<sub>2</sub> results in a strong interface between epoxy and ND- NH<sub>2</sub> and a smoother transition in frictional forces.

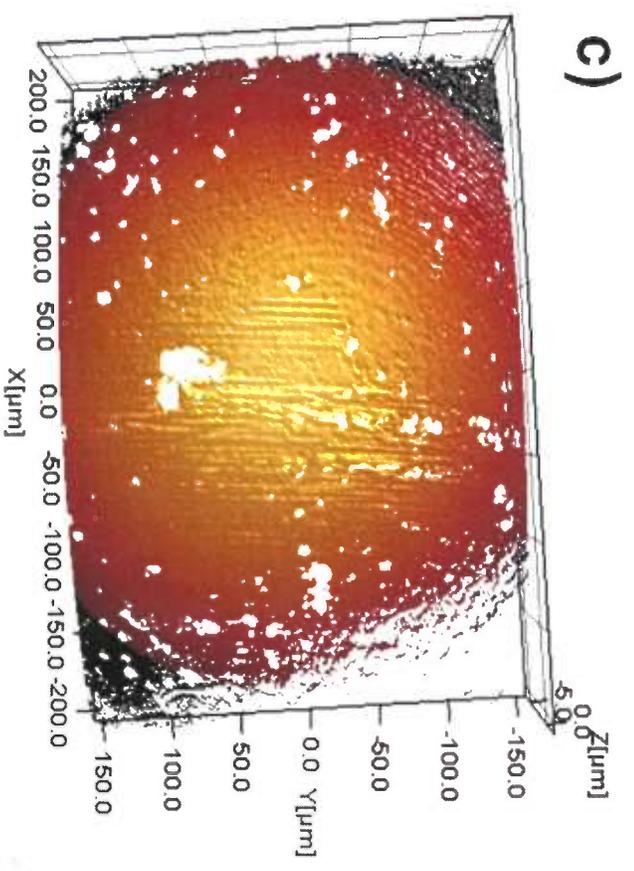
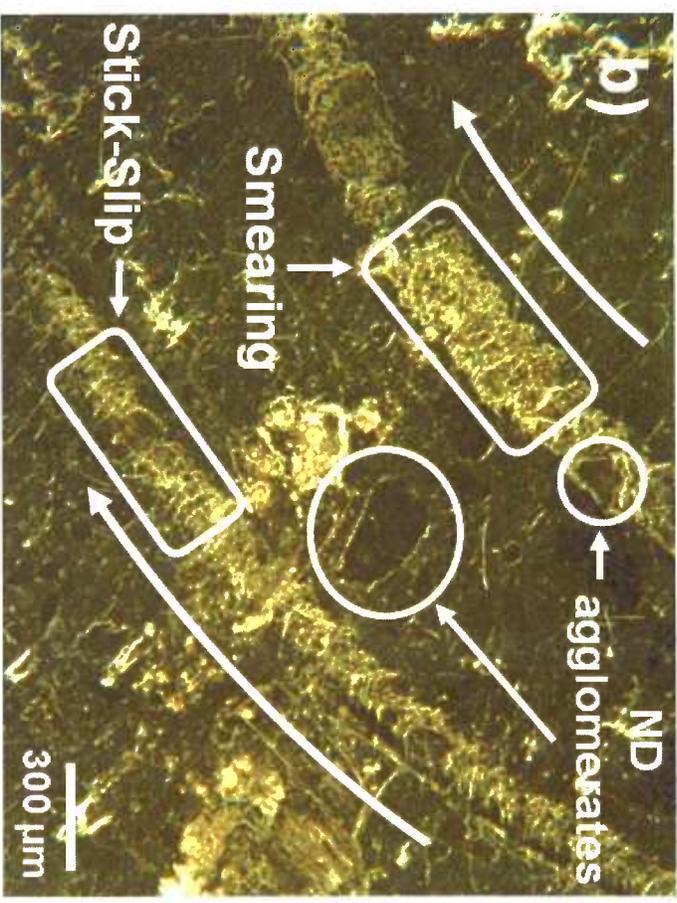


Fig. 1

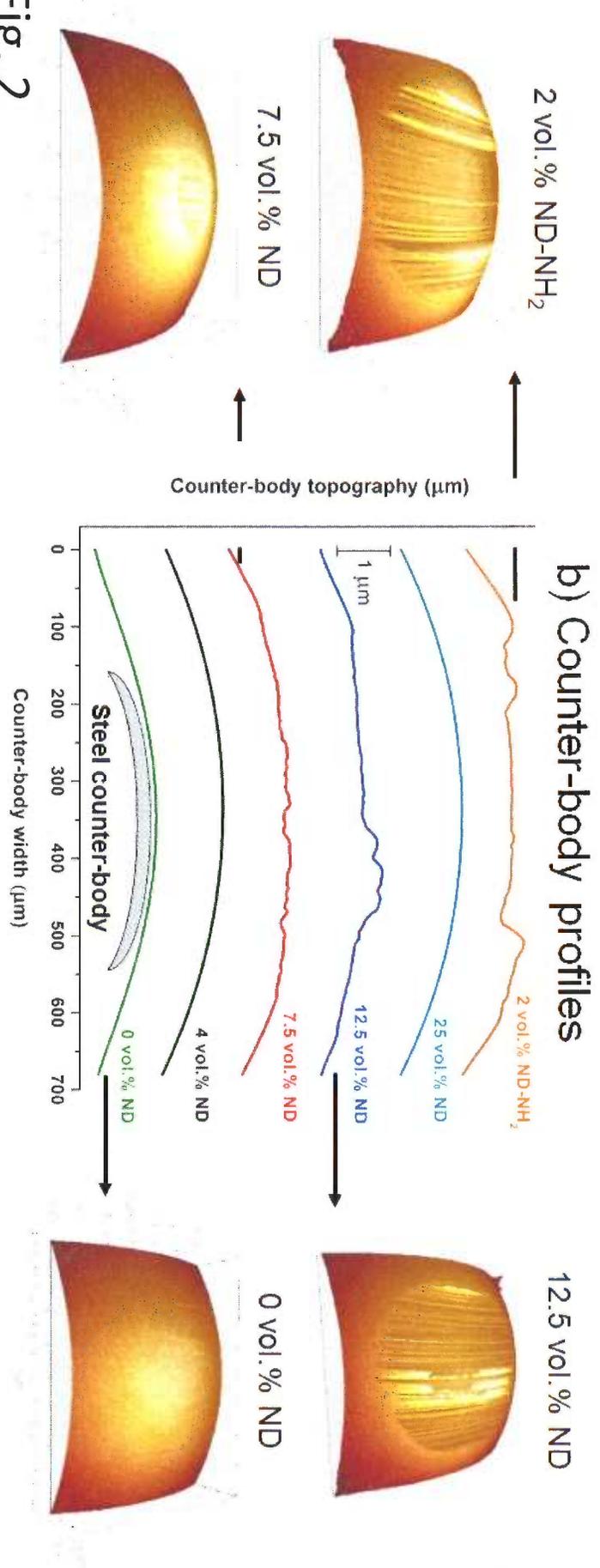
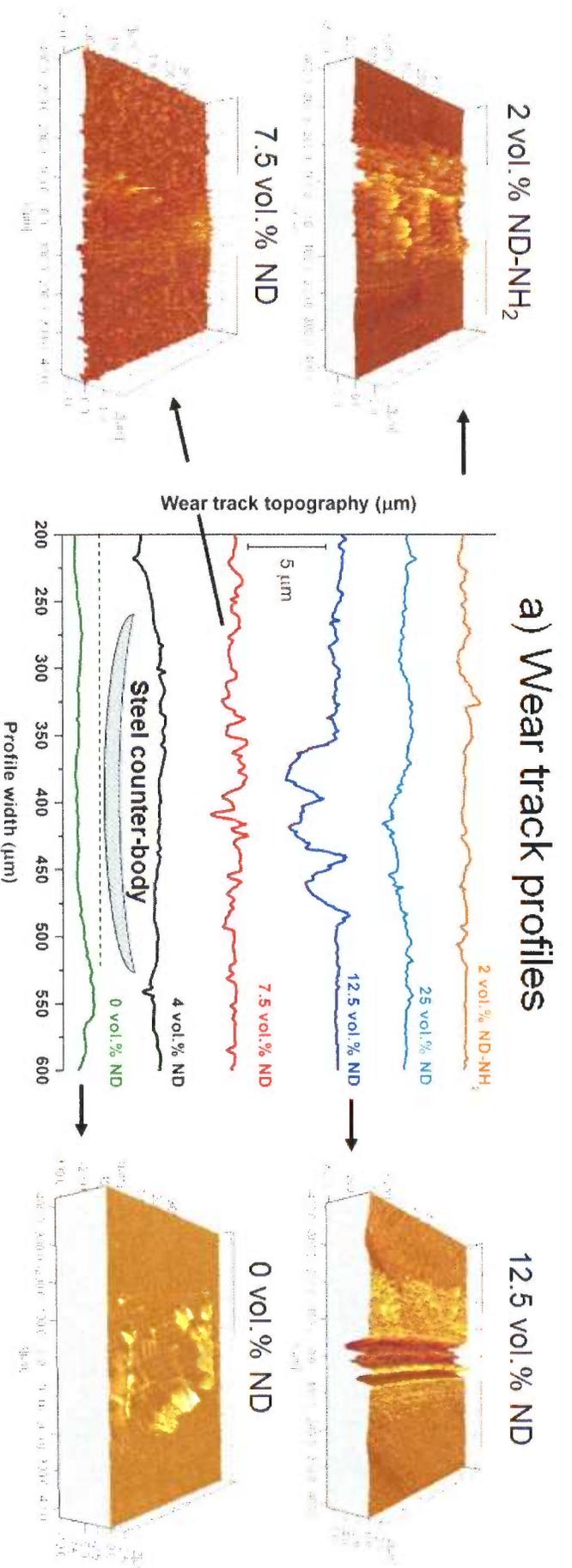


Fig. 2

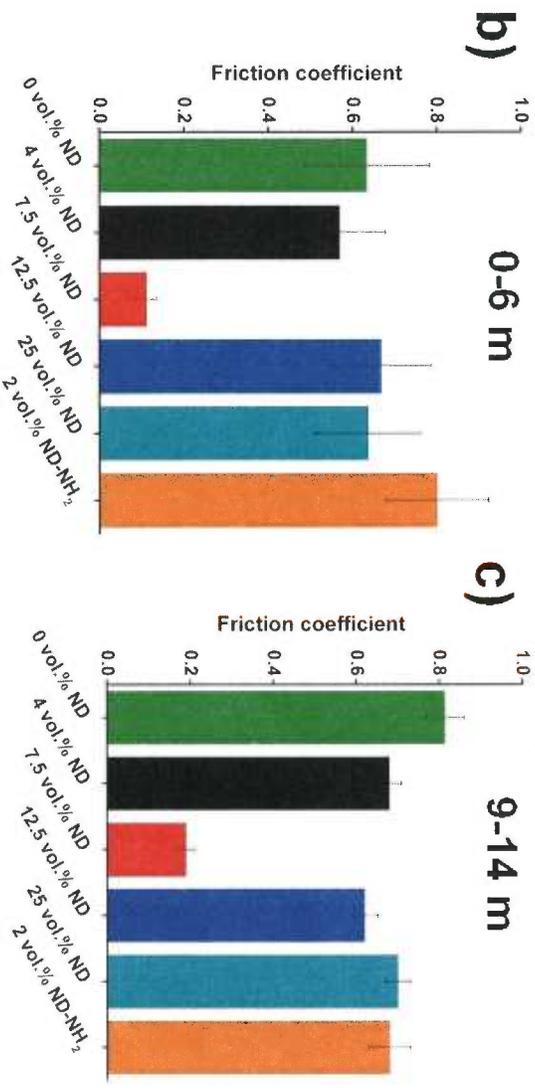
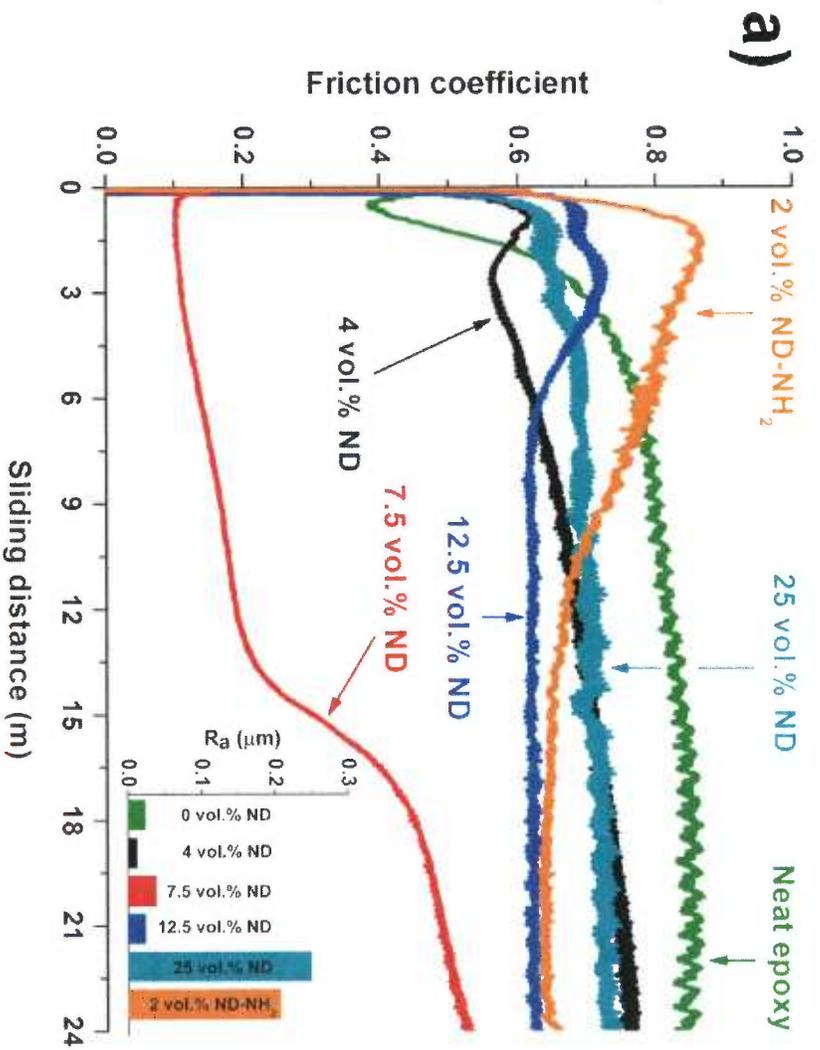


Fig. 3

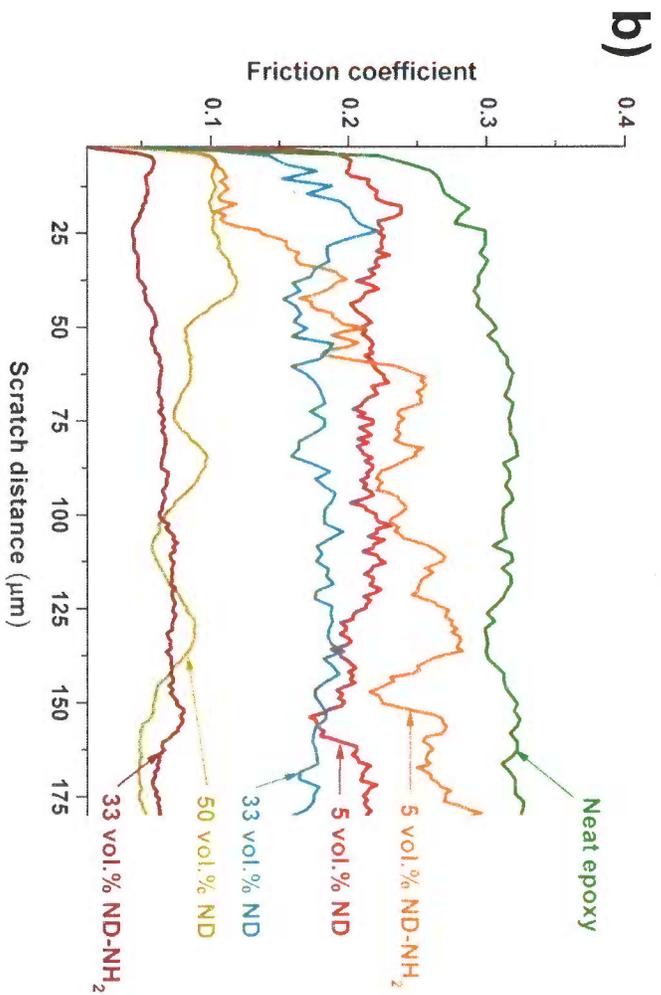
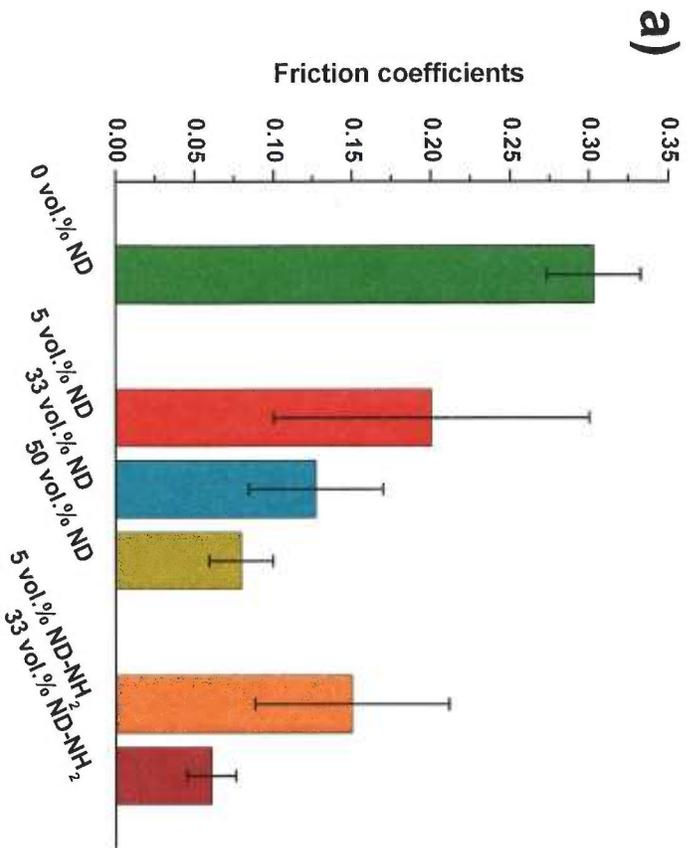


Fig. 4

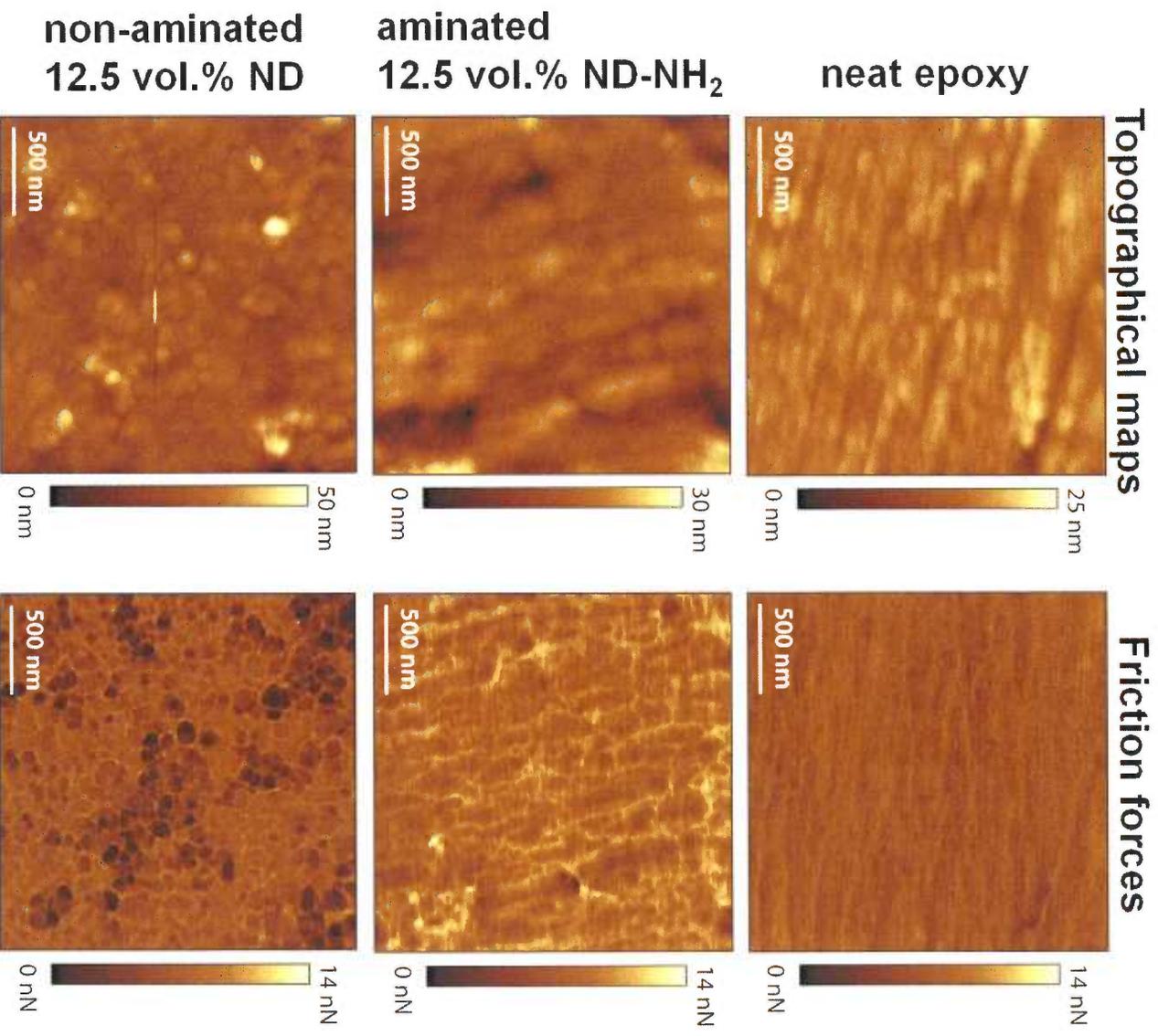
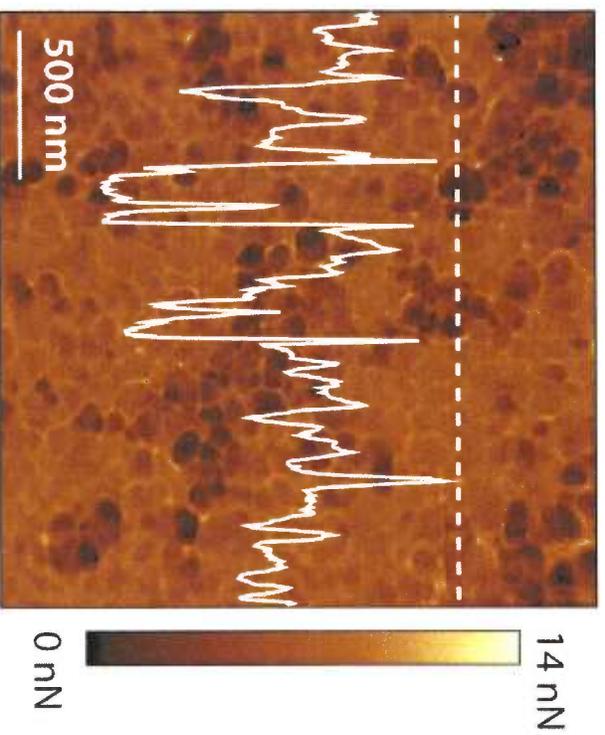


Fig. 5

a) Non-aminated 12.5 vol.% ND



b) Aminated 12.5 vol.% ND-NH<sub>2</sub>

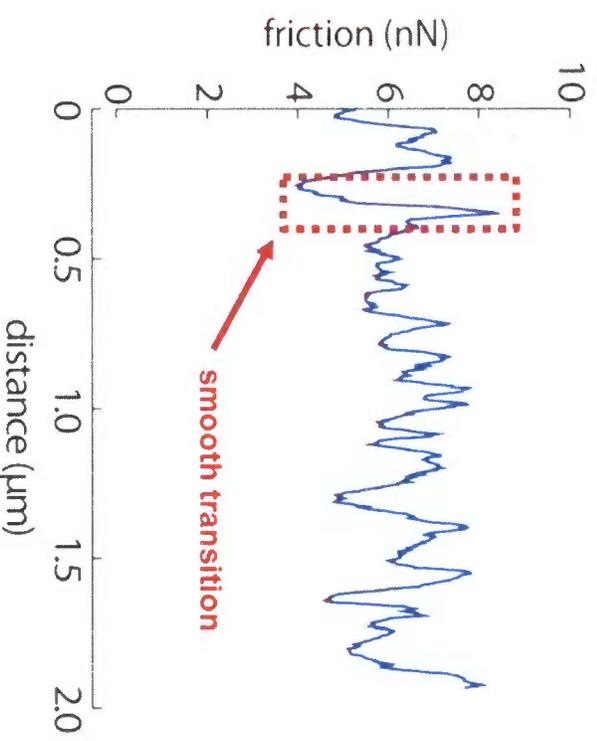
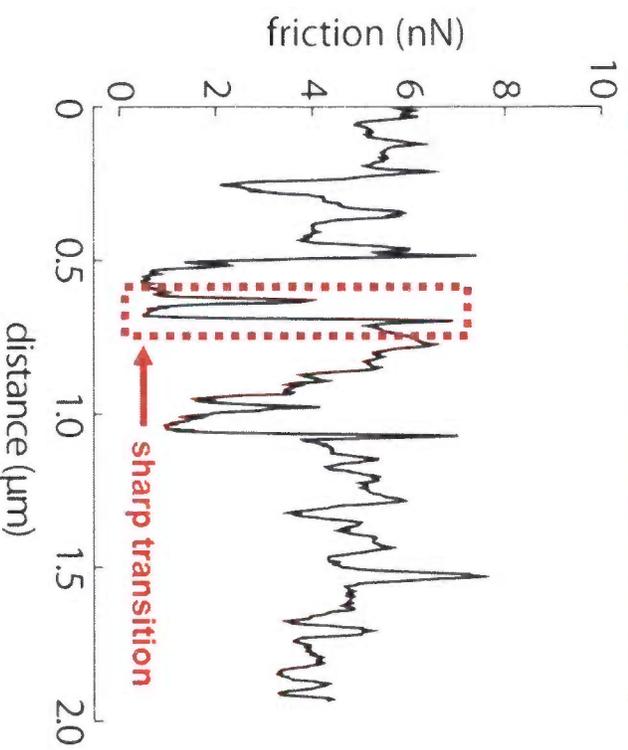
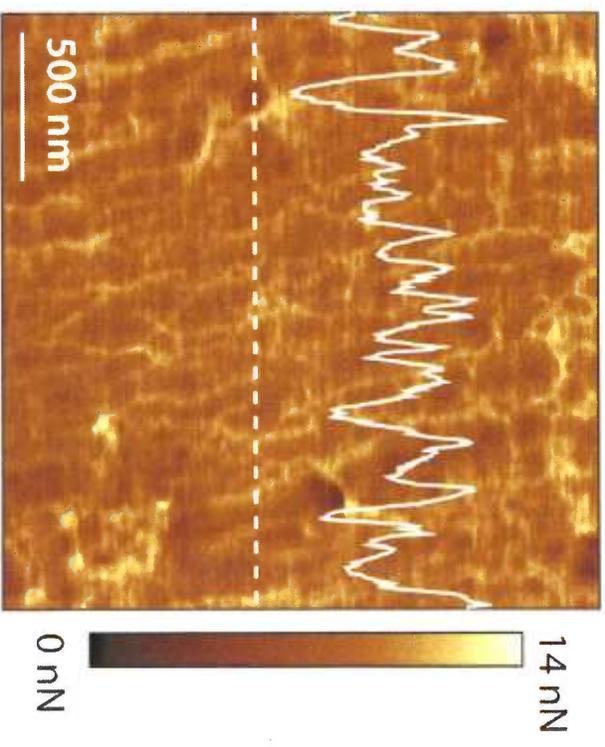


Fig. 6