

# Silica Adhesion on Toner Surfaces studied by Scanning Force Microscopy

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## Abstract

After blending with commercial available pyrogenic silicas commercial available toners based on polystyrene-acrylics or polyesters have been studied by Scanning Force Microscopy (SFM). The focus is on the simultaneous mapping of topographic features and adhesion. For this purpose, dynamic SFM techniques like Tapping Mode (TM) and Pulsed Force Mode (PFM) are used for imaging and modeling of toner surfaces and toner-silica particle interactions.

Topographic images of toner particles of different toner binder compositions were recorded. In the topographic images the toner surface are mapped as a rough surface. To localize the hard silica particles phase images are used.

To study systematically resin surface interactions a model system has been elected: a blend of polystyrene (PS) and polymethylmethacrylate (PMMA) may simulate polystyrene-acrylics toner particle surfaces. Due to its chemical composition and its dimension a Si-SiO<sub>2</sub> SFM tip can be used as a model for a silica particle. PFM is a suitable tool to investigate adhesive interactions between this Si-SiO<sub>2</sub> tip and the polymer surface. Silanization of a Si-SiO<sub>2</sub> tip has been proofed to provide a realistic model of silica particles in a silica toner system.

## Introduction

Pyrogenic silicas are key ingredients in electrophotographic toners and developers. They enhance flow and support triboelectric charging. A typical toner formulation consists of organic resin particles, colorants, waxes, charge additives. In the final process step the toner particles are blended with the surface additive pyrogenic silica. A long-term stability of the toner performance is one of the most importance requirements. The adhesion of silica particles on toner particles contributes in a significant extent to the overall performance.<sup>1-2</sup>

One crucial topic is to visualize the distribution of silica particles and the silica particle size distribution on toner particle surfaces. Scanning Force Microscopy (SFM) is an effective tool for these investigations. The SFM enables to image surface topography on nanometer scale; basic princi-

ples of these techniques are described in Refs. 3 through 6. Imaging delicate, soft samples like polymers or resins in Contact Mode can be difficult because surfaces are destroyed by applied shear forces. The development of dynamical techniques like Tapping Mode or Pulsed Force Mode, where the tip is periodically brought into contact to the surface during the imaging process<sup>5,7,8</sup> facilitate the investigation of these delicate polymer samples. One of the advantages of SFM is that at the same time contour surface plots and surface properties like local compliance or adhesion can be monitored.<sup>8-10</sup> Most recently silica toner surfaces have been investigated by this technique.<sup>7</sup> Polystyrene-acrylic toner surfaces show two distinct domains of different compliance.

The focus of this study is on the characterization of the toner surface morphology, the description of the morphology of toner-silica interfaces and the determination of adhesion forces at toner-silica interfaces. Hence, one aim of this paper is to model and investigate the interaction between the silica particles and polystyrene-acrylic toner surfaces.

## Experimental

### Samples

- Toner: monocomponent magnetic; resin: styrene-acrylic;  $d_{50}=13\ \mu\text{m}$ ;  $T_{\text{soft}}=100^\circ\text{C}$
- Toner: nonmagnetic; color (magenta); resin: polyester-epoxy;  $d_{50}=12\ \mu\text{m}$ ;  $T_{\text{soft}}=95^\circ\text{C}$
- Pyrogenic (Fumed) Silica WACKER HDK: H05TX, H30TX (surface treatment: polydimethylsiloxane/hexamethyldisilazane PDMS/HMDS) HDK H05TM, H30TM (surface treatment: hexamethyldisilazane HMDS):  
tribocharge: negative

### SFM Measurements

For all measurements a commercial stand-alone SFM (D3100, Veeco Instruments, Santa Barbara) was used. Images were performed under ambient conditions. To image silica toner particles Tapping Mode with phase imaging has been used. Used silicon tips have a resonance frequency of 270 kHz and a tip radius of about 10 nm. Images are per-

formed with an amplitude damping of about 75 %. In phase images differences in phase shifts are mapped as different colors. Working in the repulsive force regime, darker areas can be correlated to softer materials and bright areas to harder materials.

Silica-toner interactions were studied by adhesive force measurements in Pulsed Force Mode. The PFM based on the continuous recording of force vs. distance curves<sup>11</sup> developed by van der Werf.<sup>12</sup> In contrast to these experiments in PFM a sinusoidal z-modulation is used to perform force vs. distance curves.<sup>13</sup> Typical modulation frequencies ranging from 100 Hz to 2 kHz and typical modulation amplitudes are between 100 nm and 1  $\mu$ m. Resulting force vs. time curves are shown in figure 1.

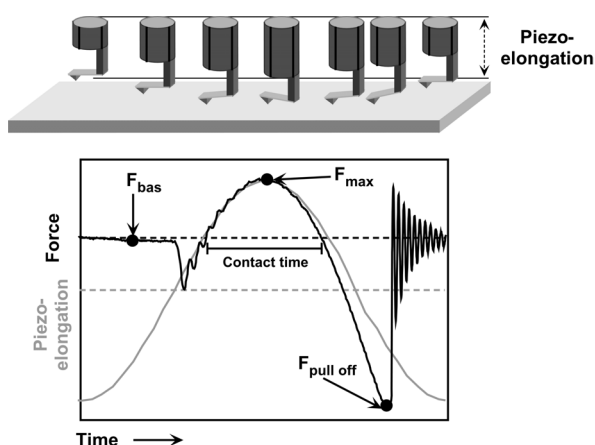


Figure 1. Resulting force vs. time curves

The PFM allows an exact determination of the forces applied to the surface during the whole sine period. Thus, surface properties like local compliance or local adhesion can be determined more quantitatively. The PFM automates the measurement of topography and surface properties at every point on the sample surface by recording a few characteristic points of the curve. Data that taken from the curve are the maximum force ( $F_{max}$ ), which reflects the topography, and minimum force, so-called force pull-off force ( $F_{adh}$ ), which can be correlated to the local adhesion.

In our experiments the modulation amplitude was 200 nm at a frequency of 860 Hz. Silicon cantilever with spring constant of about 2 N/m and a tip radius of about 10 nm are used.

### SFM Sample Preparation

It has been shown that preparing the samples out of an ethanolic suspension leads to removal of silica particles from the toner particles.<sup>7</sup> More realistic sample are provided by dispersing particles directly on a support. To avoid the

displacement of the particles during SFM imaging, they have to adhere properly on the supporting surface. Sticky tapes are not suitable as a adhering substrate because the adhesive polymer matrix of the tape cover the particles after few hours,

For our study toner particles or silica toner particles are dispersed on a ultraflat silicone rubber sheet. The rubber sheet is prepared by spreading the precursor on a silanized Petri glass dish. After curing the rubber sheet is removed from the glass. The rubber in contact with the glass provides a roughness below 3 nm useful as a sample support.

### Model Systems

To study systematically resin surface interactions models have been selected: as a model of polystyrene acrylics toner particles a blend of polystyrene (PS) and polymethylmethacrylate (PMMA) is used. The tip of the SFM cantilever can be used as a model system for silica particles. Usually under ambient conditions silicon cantilever are covered with SiO<sub>2</sub>. Furthermore the curvature of the silicon tip is about 10 nm; which is in the same dimension as primary particles in a pyrogenic silica aggregate of about 100 nm. This enables to use the tip as a model for silica particles. Commonly, the pyrogenic silicas used as free flow and charging additives in toners are so-called surface modified silicas. For that reason, a surface modified Si-SiO<sub>2</sub> tip would provide a more realistic picture of the toner silica interactions.

### Modelling the Toner-Resin Surfaces

A blend of polystyrene (PS) and polymethylmethacrylate (PMMA) is applied as a model of polystyrene acrylics toner particles. To study tip-surface interactions on nanometer scale smooth surfaces are necessary. Spin-coating is a suitable method to prepare smooth polymer surfaces. Here, a droplet of a polymer solution is put onto a rotating silicon substrate.

### PS/PMMA Blends

10 mg polymer are solved in 1 ml toluene. Mixing 3 ml of PMMA solution and 1 ml of PS solution leads to a phase separated film providing PS islands on a PMMA film.

### Tip Modification by Silylation

Tapping Mode and PFM cantilevers are silanized ie. hydrophobized either by putting the cantilever in the saturated atmosphere of HMDS for 6 days or by immersing them into a 2 % solution of dimethyldichlorosilane (PDMS) in toluene for 2 hours. Typically hydrophobization is proofed by measuring the contact angle of the sample after modification. Due to the small size of the tips the contact angle can not be estimated. Thus, concurrent to the cantilever small pieces of a silicon wafers are modified to enable the of contact angle measurements.

## Results and Discussions

### Polyester Toner Silica Free

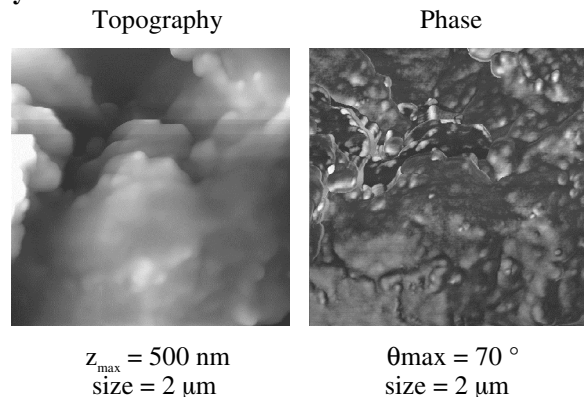


Figure 2a, b. Topography and phase of silica free polyester toner

### Polystyrene-Acrylics Toner Silica Free

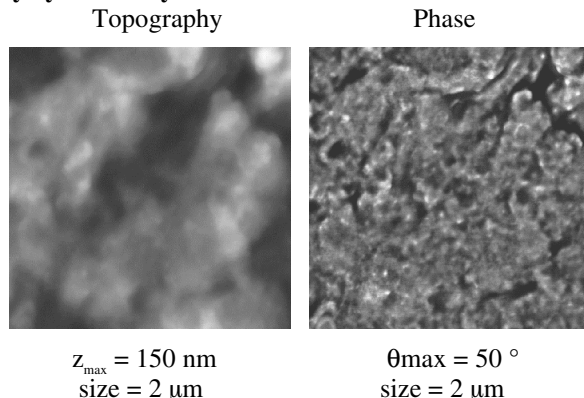


Figure 2c, d. Topography and phase of silica free polystyrene-acrylics toner

Figure 2 a - d: show silica free toner surfaces of polyester (magenta) toner and polystyrene-acrylics (black) topography and phase shift. Both toner particles appear to be rough, showing edges and surface textures. The morphology of the toner particles can be related to the conventional toner manufacturing (crushing). Domains of different phase shift indicate polymer phases of different compliance.

### Silica-Loaded Toner Surfaces

On the toner surfaces silica particles can be detected by significantly higher phase shifts. The sizes of these silica particles on the toner surface are in the range of about 100 – 200 nm. Comparing PDMS/HMDS and HMDS modified silica particles, a lower phase shift up to  $90^\circ$  has been observed for the PDMS/HMDS silicas and for the HMDS silicas a higher phase shift up to  $120^\circ$  have been found. Differences in phase shift values indicate the impact of surface modification on the local hardness of the silica particles. "PDMS" modification leads to a softer, polymer like grafting whereas pure HMDS modification only increases

the hydrophobicity by a hard monolayer formation of trimethylsiloxy groups. HMDS treated silicas seemed to interact weaker with the toner resin surfaces. Thus, silica particles to the tip attach easily to the tip resulting in images with poor resolution. In contrast, PDMS/HMDS treated silicas show stonger adhesion to the toner resin surfaces that case that they can easily be image with relatively high resolution.

### Polyester Toner Loaded with 0.5 wt% Silica; BET50 $\text{m}^2/\text{g}$

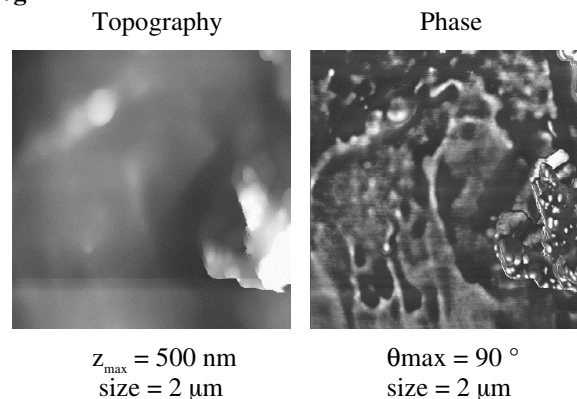


Figure 3a,b. Topography and phase of polyester toner loaded with 0.5 wt% silica; BET:  $50 \text{ m}^2/\text{g}$ ; HMDS/PDMS treated; WACKER HDK H05TX

### Polyester Toner Loaded with 0.5wt% Silica; BET300 $\text{m}^2/\text{g}$

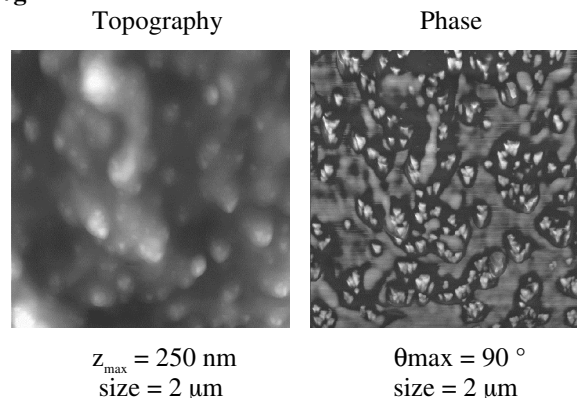


Figure 3c,d. Topography and phase of polyester toner loaded with 0.5 wt% silica; BET:  $300 \text{ m}^2/\text{g}$ ; HMDS/PDMS treated; WACKER HDK H30TX

Figure 3 a – d: show toner surfaces of polyester (magenta) toner topography and phase shift loaded by silicas of 50 and 300  $\text{m}^2/\text{g}$  ie which we relates to bigger and smaller silica particles.

Comparing surface particles with different BET shows that in general, low BET surface particles ( $50 \text{ m}^2/\text{g}$ ) adhere markedly weaker than higher BET surface particles ( $300 \text{ m}^2/\text{g}$ ). Which results in lower numbers of silica particles at

the toner surface as well for the polyester toner as for the Polystyrene-acrylics toner (figure 4 a-d).

#### Polystyrene-Acrylics Toner Loaded with 0,5 wt% Silica; BET 50 m<sup>2</sup>/g

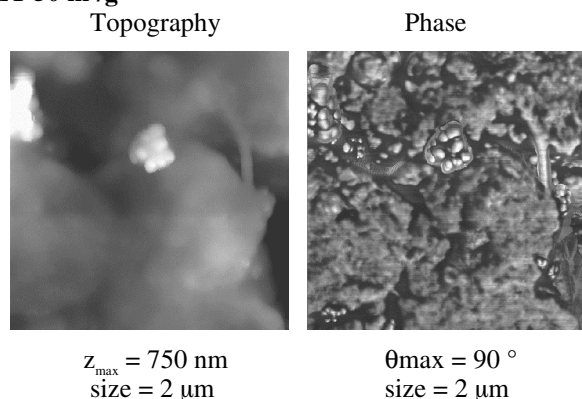


Figure 4a,b. Topography and phase of polystyrene-acrylic toner loaded with 0.5 wt% silica; BET: 50 m<sup>2</sup>/g; HMDS/PDMS treated; WACKER HDK H05TX

#### Polystyrene-Acrylics Toner Loaded with 0,5 wt% Silica; BET 300 m<sup>2</sup>/g

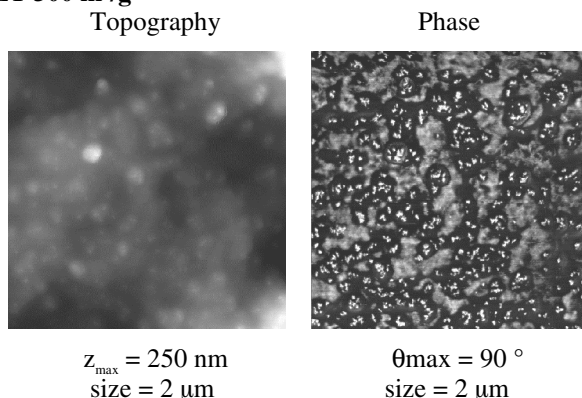


Figure 4c,d. Topography and phase of polystyrene-acrylic toner loaded with 0.5 wt% silica; BET: 300 m<sup>2</sup>/g; HMDS/PDMS treated; WACKER HDK H30TX

Figures 3 d, 4 d show phase images of toner surfaces loaded by silicas of 300 m<sup>2</sup>/g. In all cases the silica particles on the toner resin surfaces are surrounded by darker rims or regions. This indicates regions of lower compliance. We propose that this effect could be a particular interaction of the PDMS/HMDS silica surfaces with the surrounding resins. Because the comparison with HMDS modified silicas do not show these softer domains close to silica particles a tip artefact can be excluded.

#### Modelling Silica Toner Interactions

We chose a Si-SiO<sub>2</sub> tip and films of a PS/PMMA blend as a model system for the investigation of the silica particle-polystyrene-acrylic toner surface interactions. Due to its chemical composition and its dimensions the Si-SiO<sub>2</sub> tip models the silica particles. The PS/PMMA blend reflects the

two-phase morphology of the polystyrene-acrylic toner surface.

Tapping Mode is applied to investigate the phase-separated structure of the PMMA/PS blend. In figure 5 a,b topography and phase image of a PMMA/PS blend spin coated on a silicon substrate are shown. Both the contour and the phase image displayed the two-phase morphology. The topography image shows islands of one polymer deposited on the other. These elevated regions can be attributed to PS domains. These domains show larger phase shift than the lower PMMA areas.

#### Non-Treated Silicon Tip

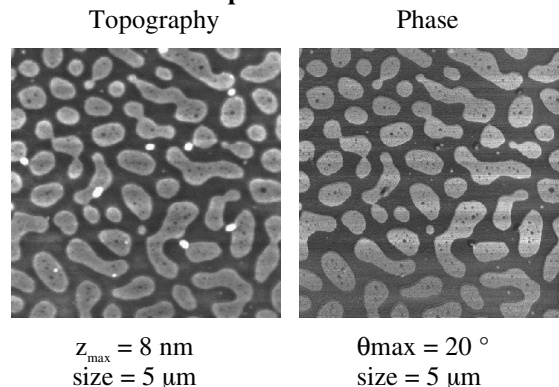


Figure 5a,b: Topography and phase of a blend of polystyrene (PS) and polymethylmethacrylate (PMMA)

To check if a silylation by dimethyldichlorosilan leads to a permanent modification of the tip, the same polymer blend is mapped with a silanized tip. Topography and phase images are very similar to the ones taken with the non-modified cantilever. This confirms that the tip modification is permanent. Again, the elevated areas show higher phase shift. But the maximum value of the phase shift has been decreased from 20° to 10°. This decrease in phase shift after modification indicates variations in the tip surface interaction.

#### PDMS Treated Silicon Tip

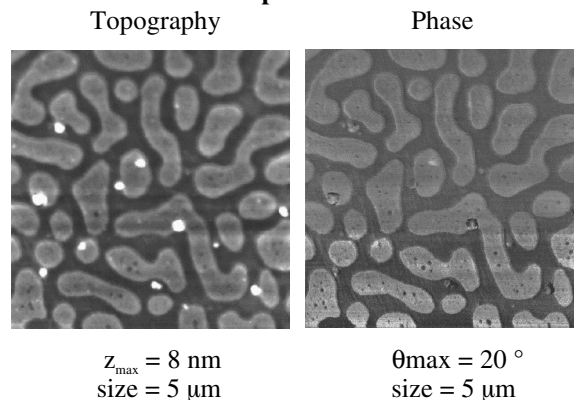


Figure 5c,d: Topography and phase of a blend of polystyrene (PS) and polymethylmethacrylate (PMMA; tip surface treated with dimethyldichlorosilane (PDMS))

Phase shift mainly reflects the dissipation of energy while the tip is in contact to the surface. The influence of mechanical and chemical surface properties in the phase signal can not be differentiated. Thus, Tapping Mode is not a suitable technique to investigate tip-sample interactions on a more quantitative level. In PFM the force can be controlled and recorded while the tip is in contact to the sample surface that case that specific forces like the pull-off force can be monitored separately. This allows a direct correlation to the interaction between tip and surface.

Figure 6 shows the topography and the adhesive force image of the PS/PMMA blend imaged by a non-sililated cantilever in PFM. The topography image shows a two-phase morphology similar to the one recorded in Tapping Mode. The elevated PS domains appear to be brighter in the adhesive force image indicating stronger interactions between PS and the Si-SiO<sub>2</sub> tip.

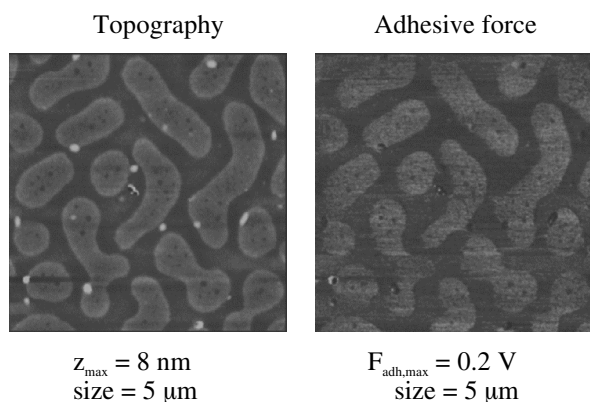


Figure 6a,b: Topography and adhesion force of a blend of polystyrene (PS) and polymethylmethacrylate (PMMA); non treated tip

Treating the cantilever with HMDS or dimethyldichlorosilane which leads to short PDMS chains after silylation PDMS did not change topography images (figure 6 c-e). Thus, similar as for Tapping Mode silylation leads to permanent modification of the tip and enables the steady imaging of surfaces in PFM. After surface modification the contrast in the adhesive force image is inverted that case that the elevated PS domains appears dark. Thus, silanization increases the interactions between PMMA and tip. Comparing HMDS and PDMS modification show higher adhesive forces (0.25 V) for the PDMS modified tip than for the HMDS modified (0.15 V). This indicates stronger interactions between a PDMS modified tip and the polymer surface than between a HMDS modified tip and the polymer surface.

This effect can be explained either due to a difference in the chemical composition of the surface or due to a change in tips radius. HMDS modification only increases the hydrophobicity of the tip forming a hard monolayer of trimethylsiloxy groups. Due to steric reasons this monolayer is not perfectly closed. In contrast "PDMS" modification leads to a polymer like grafting which can increase the tip radius. It is know that increasing the tip radius will also

increase the measured pull-off force. To attribute the difference in measured adhesive force to one of these effects further experiments are necessary.

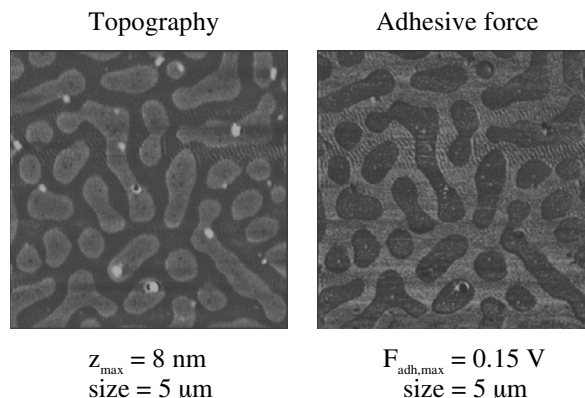


Figure 6c,d: Topography and adhesion force of a blend of polystyrene (PS) and polymethylmethacrylate (PMMA); HMDS treated tip

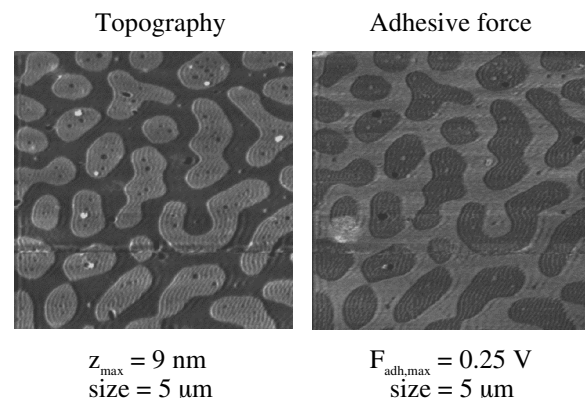


Figure 6e,f: Topography and adhesion force of a blend of polystyrene (PS) and polymethylmethacrylate (PMMA); dimethyldichlorosilane treated tip

## Conclusion

According to our findings smaller silica particles of higher BET surface area adhere stronger on the toner resin surface in comparison to larger silica particles of lower BET.

For toner systems surface modified silicas are used. Therefore, studying the adhesion forces of silica with toner resins requires surface modified Si-SiO<sub>2</sub> in PFM. Our results show that surface modified tips allows steady imaging of polymer blends with respect to the adhesive properties. Additionally, comparing the non-modified to the modified tips shows even an inversion of the strength of interactions can be observed.

Changing surface modification from Trimethylsiloxy-groups to polymer-like grafted PDMS seems to have a market impact on silica toner resin interactions. HMDS modified silica particles tend to stick on the cantilever tip, and being removed from the toner resin surface during image recording; in contrast silicas particles modified by PDMS

can be steadily imaged on the toner resin surface. Additionally, PDMS modified silica particles on the resin surface are surrounded by zones of weaker compliance indicating a specific interaction - also a PDMS coated Si-SiO<sub>2</sub> tip shows higher adhesion forces on PMM/PS folies compared to the HMDS treated tip.

Further studies will be dedicated to quantify interactions of surface modified tips with different kinds of polymer films and relate these data to existing toner resin particles including chemical prepared toners. These studies will include different kinds of silica surface modification.

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### Biography

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