Adhesion of Silica Particles and Silylated Silicon Tips on Model Toner Surfaces – A SFM Study

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Abstract

Toner flow and tribochargeability are strongly influenced by pyrogenic silica particles, depending on the surface chemistry of the pyrogenic silica particles and their particle dimensions. Scanning Force Micorscopy (SFM) is an effective tool to describe surface features and mechanical properties of toner particles. Conventional toners based on polystyrene (PS) and polymethylmethacrylate (PMMA) and polyester are used; in addition the study covers chemical prepared toners (CPT) as well. Pyrogenic silica particle geometries have an impact on the pyrogenic silica-toner adhesion. Combining smaller and larger pyrogenic silica particle dimensions together with different surface chemistries, providing harder and softer silylation layers, enables to develop models of real pyrogenic silica toner 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-pyrogenic silica particles.

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 and charge additives. The conventional toners manufacturing process starts with melt - mixing of the ingredients, grinding and classifying lead to the required toner particle size. Whereas the CPT – process starts from the monomer or aggregation level of the resin, controlled growth including the implementation of the internal additives in a liquid dispersion phase lead to the required particle size. CPTs per se achieving smaller particle dimension in comparison to conventional toners. The characteristic rough surface of conventional toners due to the process conditions has been transformed to more smooth surfaces. The shape of CPTs are more spherical in comparison to conventional toners. However, CPTs are not limited to a spherical shape. In the final process step of toner either conventional or CPT based the toner particles are blended with flow enhancers and external charge controllers; in most cases pyrogenic silicas. The long-term stability of the toner performance in terms of charge stability and high flow even under high temperature and humidity is one of the most challaging requirements. The adhesion of pyrogenic silica particles on toner particles contributes in a significant extent to the overall performance.[1,2]

The shape of the toner particles, their surface chemistry and surface energy have an impact on the system pyrogenic silica-toner.

One crucial topic is to visualize the distribution of pyrogenic silica particles and the pyrogenic silica particle size distribution on toner particle surfaces. SFM is an effective tool for these investigations. The SFM enables to image surface topography on nanometer scale; basic principles of these techniques are described in Refs. [3-6]. The development of dynamical techniques like Tapping Mode (TM) were the tip is periodically brought into contact to the surface during the imaging process.[7,8] facilitate the investigation of these delicate polymer samples. In TM the topography is measured as the constant distance of the tip normal to the surface by keeping the amplitude of the oscillating tip constant. The level of the force applied to the surface is given by so called amplitude damping r_{SP}. r_{SP} is defined as the magnitude of the engaged amplitude to the free air amplitude (A_0) of the oscillating tip $r_{SP} = A/A_0$. Assuming that the oscilation of the cantilever is damped similarly at all sample location, height data are complemented with simultaneously measured phase shift data.[8] The phase image outlines domains of varying material contrast at or near the surface. Depending on the chosen r_{SP} the phase contrast can either be dominated by the adhesive properties of the surface or by the stiffness due to the choosen experimental parameters. Adjusting the set point ratio below 0.8 results in stiffness dominated contrast in the phase image.

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. Most recently silica toner surfaces have been investigated by this technique.[7,13]

The focus of this paper is on the characterization of the toner surface morphology, the description of the morphology of toner-pyrogenic silica interfaces and the determination of adhesion forces at toner-silica interfaces. Whereas the toners comes from different routes, conventional toners and a CPT.

Experimental

Samples

- Toner: nonmagnetic; color (magenta); resin: polyester-epoxy; d_{50}=12 µm; T_{soft}= 95°C
- Toner: nonmagnetic; b/w: CPT – technology; d_{50}=8µm
- Toner: monocomponent magnetic; resin: styrene-acrylic; d_{50}=13µm; T_{soft}=100°C
- Pyrogenic (Fumed) Silica WACKER HDK:
  H05TX (BET hydrophilic base silica: 50 m²/g),
  H30TX (BET hydrophilic base silica: 300 m²/g) surface treatment: polydimethylsiloxane/ hexamethyldisilazane PDMS/HMDS
  H05TD (BET hydrophilic base silica: 50 m²/g),
  H30TD (BET hydrophilic base silica: 300 m²/g) Surface treatment: polydimethylsiloxane PDMS
  H05TM (BET hydrophilic base silica: 50 m²/g),
  H30TM (BET hydrophilic base silica: 300 m²/g) Surface treatment: hexamethyldisilazane HMDS
  All pyrogenic silicas showed a high negative tribocharge (q/m; blow-off from ferrite)

SFM Measurements

A Nanoscope D3100 Scanning Force Microscope (Veeco Instruments, Santa Barbara, CA) has been applied to acquired the images. Pictures are taken under ambient conditions (30% humidity; 278 K) in tapping mode using standard microfabricated silicon cantilever with aluminium reflex coating (Olympus, AC160TS). In our studies the free amplitude has been set to 2 V and the amplitude damping r_{SP} is adjusted to 0.65 – 0.7 (1.325 – 1.35 V) which is suitable and moderate force for imaging. Under these conditions a high phase shift corresponds to high stiffness regions of the sample. In this case, higher phase shift, noticeable as brighter regions of the samples, can be attributed to harder areas of the samples. To receive a better impression on the surface morphology the images are subjected to a second order surface flattening process. After this procedure the primary spherical topography appears flat. Details, like attached silica particles can be better identified.

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. More realistic samples are provided by dispersing particles directly on a support, like sticky tape. To avoid the displacement of the particles during SFM imaging, they have to adhere properly on the supporting surface. One possibility is to disperse them by air flow on sticky tapes (Tesa, double sided, Beiersdorf). Because the adhesive polymer matrix of the tape covers the particles after one day of storage images has to be taken only on freshly prepared samples.

Blending Impact

To evaluate the impact of the blending conditions a low shearing blender (Turbula) and a high shearing blender (Henschel-type) has been used.

Results and Discussions

1. Conventional Toner Systems

Styrene-Acrylic Based Toner Silica Free

The conventional styrene-acrylic resin show a rock-like structure leading to a surface morphology with step edges up to several 100 nm height and plateaus up to 2 µm lateral extension. On the plateaus only small variations in height can be found. The phase shift image of such a plateau region show a inhomogeneous morphology. The main part of this areas appears dark with an averaged phase shift of about 30, indicating the softer area. This area contains bright spot of about 50 nm dimensions with a phase shift of about 40° showing hard domains. This indicates a phase separated structure of softer acrylic areas (dark) and harder polystyrene domains.

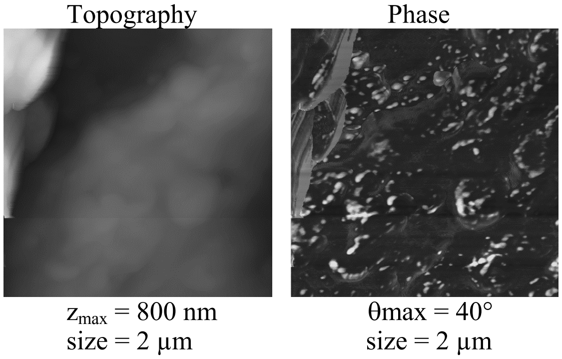


Figure 1. Topography and phase of silica free PS/PA toner

Polyester Toner Silica Free

The overall shape of this toner is more rotund and the surface of its is less rough than the styrene-acrylic one without sharp edges. The phase images show maximum phase shift of about 35°. Only small variations in phase shift can be detected pointing to a mainly homogeneous surface.

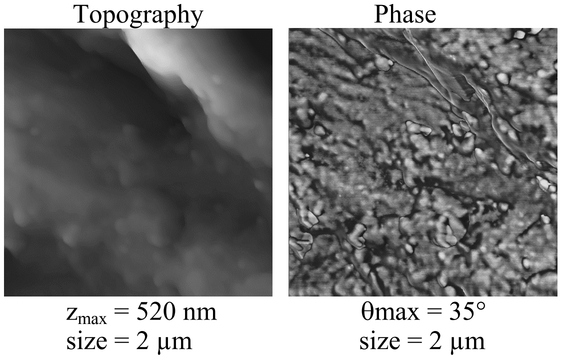
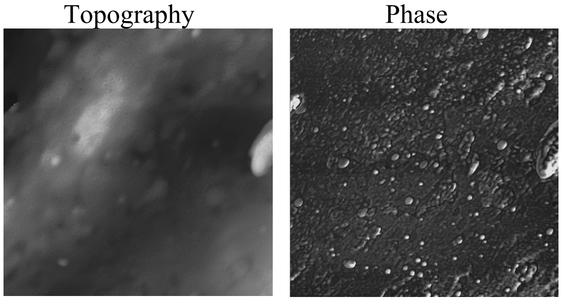


Figure 2. Topography and phase of silica free polyester toner

2. Chemical Prepared Toner Silica Free

The CPT show a nearly spherical shape with a smooth surface. The maximum height is at 100 nm. The maximum phase shift of about 26° is smaller than both of the other investigated resins. This indicates a soft surface. In the phase image s granular structure of about 50 to 100 nm can be seen, which might be due to the synthesis process.



z_{max} = 100 nm θmax = 26°
size = 2 µm size = 2 µm

Figure 3. Topography and phase of silica free chemical prepared toner

Figure 2, 3 and 4 show silica free toner surfaces of different toners in topography and phase shift mode. Figure 2 exhibits a rough surface texture, figure 3 shows less roughness compare to figure 2. The toner in figure 4 exhibits smooth surface textures. Domains of different phase shift indicate polymer phases of different compliance in all three toners.

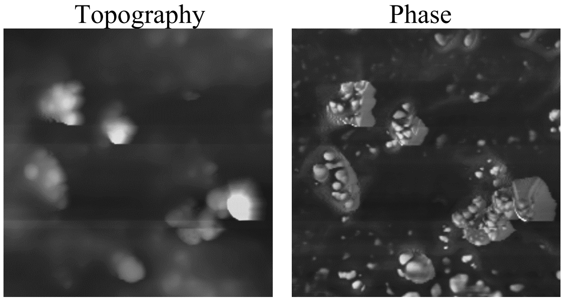
Silica-Loaded Toner Surfaces

Conventional Toners

On the toner surfaces pyrogenic silica particles can be detected due to significantly higher phase shifts. The sizes of these pyrogenic 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 70° has been observed for the PDMS/HMDS silicas and for the HMDS silicas a higher phase shift up to 90° 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 hydrohobicity 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 stronger 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; BET 50 m²/g

HMDS modified silica particles with a diameters up to 300 nm can be detected on the polyester toner surface. Even in the topography image the raspberry like substructure of the particles can be detected. These particles have only a low adhesion to the resin, thus even the extremely low lateral forces during the tapping mode scan can remove sections of the particles as can be seen in the brighter line in the upper part of the topography image. In the phase image the particles exhibit a high phase shift of about 98°. These particles are much harder than the resin. The bright brims around the particles are an artifact due to the increase contact areas between tip and polymer surface at the edges of the hard cluster.

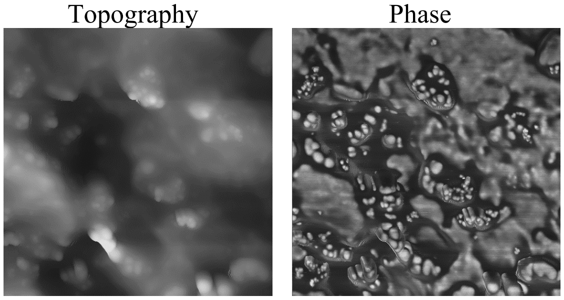


z_{max} = 330 nm θmax = 98°
size = 2 µm size = 2 µm

Figure 4a. Topography and phase of polyester toner loaded with 0.5 wt% silica; BET: 50 m²/g; HMDS treated; WACKER HDK H05TM

Polyester Toner Loaded with 0.5 wt% Silica; BET 50 m²/g

PDMS treated silica particles are less pronounced in the topography image indicating softer particles which can be compressed. This assumption is supported by the fact that the maximum phase shift is smaller than for the HMDS modified silica particles. In the phase image, aggregates of small spheres of approx. 100 nm diameter can be found. The dark seam around the particles a hint to a softer layer around the particles or cluster just as the reduced maximum phase shift. So of the cluster are surrounded by a larger, dark area indicating the softening around the particles - maybe due to interaction between PDMS and the polymer.



z_{max} = 400 nm θmax = 77°
size = 2 µm size = 2 µm

Figure 4b. Topography and phase of polyester toner loaded with 0.5 wt% silica; BET: 50 m²/g; PDMS treated; WACKER HDK H05TD

Polyester Toner Loaded with 0.5 wt% Silica; BET 300 m²/g

At the surface of the toner only isolated protrusions can be found. These protrusions can be correlated to small particles with a phase shift of about 95°. Thus, mainly isolated silica aggregates are adsorbed to the surface. The diameter of these particles is approx. 100 nm. Mostly the show a collar of about 5 nm thickness, which can be explained by decrease in contact area.

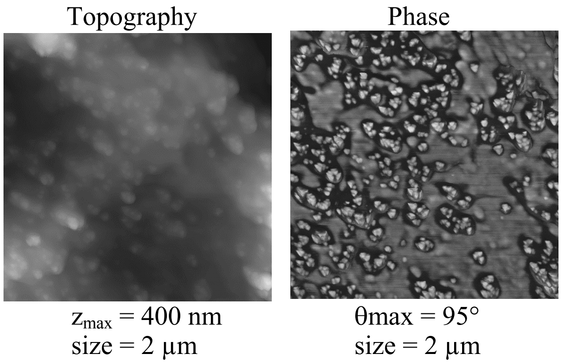


Figure 4c. Topography and phase of polyester toner loaded with 0.5 wt% silica; BET: 300 m²/g; HMDS treated; WACKER HDK H30TM

Polyester Toner Loaded with 0.5 wt% Silica; BET 300 m²/g

PDMS modified particles seem coat nearly the entire toner particle. Their topographical diameter is doubled compared to the HMDS coated particles, but the diameter estimated from phase image is very similar to the one found for the HMDS modified ones. The maximum phase shift is reduced compared to the samples above. This indicates that the particles are covered by a soft material. These soft material covers not only the particles but also the resin surface in-between them. This can be seen by the decrease phase shift in between the silica particles compared to the pure resin. Like in sample 4b, probably the PDMS interact with the toner resin surface.

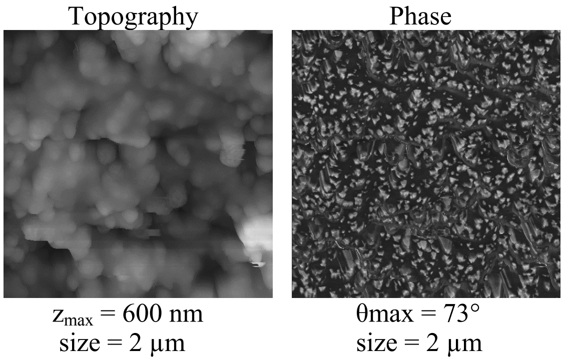


Figure 4d. Topography and phase of polyester toner loaded with 0.5 wt% silica; BET: 300 m²/g; PDMS treated; WACKER HDK H30TD

Chemical Prepared Toner Loaded with 0.5wt% Silica; BET 50 m²/g

Silica particles are visible on the surface of the chemical prepared toner as cluster with a diameter up to 500 nm. Whereas for on the polyester toner single silica aggregates are hardly to be detected, on this toner single silica's with diameter of about 100 nm can be observed even in the topography image. In the phase image these particles with a effective diameter below 100 nm show the highest phase shift, indicating that they are the hardest part of the surface. Around the particles an area with very low phase shift can be found. The dimension of this soft areas extends to 100 nm around the particles. Similar to the PDMS modified silica particles on the polyester toner, the silylated surface should interact with the toner surface. The large extension of the soft area indicates that the interactions is stronger than for the polyester resin.

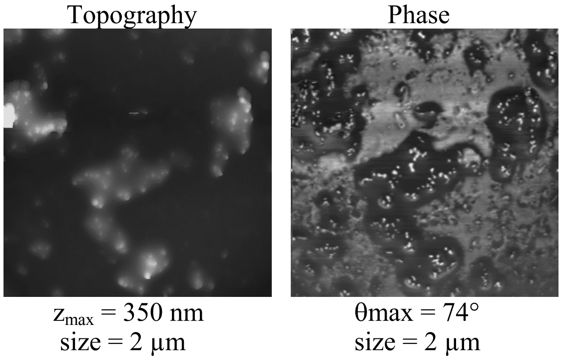


Figure 5a. Topography and phase of chemical prepared toner loaded with 0.5 wt% silica; BET: 50 m²/g; HMDS/PDMS treated; WACKER HDK H05TX

Chemical Prepared Toner Loaded with 0.5wt% Silica; BET 300 m²/g

On the surface of the toner a huge amount of aggregates can be observed which have a diameter between 100 and 200 nm. Like seen in the sample above, the particles can be correlated to bright (hard) parts of the surface. The particles are homogeneously spread over the surface. In-between the particles again a dark, soft phase can be observed. In the lower right edge of the picture a small amount of the pure toner surface can be detected. Comparing the paste shift of this area to the phase shift in-between the particles showing higher phase shift for the pure polymer. This indicates a softening due to interaction between silylated silica particles and the toner surface.

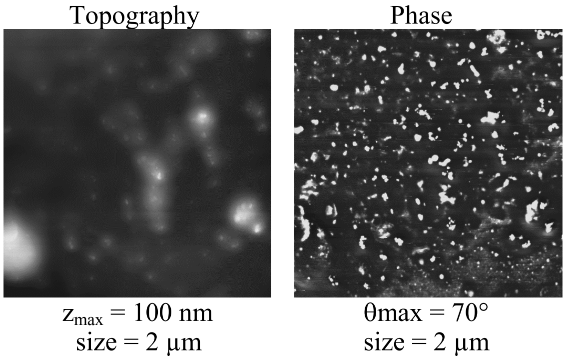


Figure 5b. Topography and phase of chemical prepared toner loaded with 0.5 wt% silica; BET: 300 m²/g; HMDS/PDMS treated; WACKER HDK H30TX

Blending Impact

Polystyrene-Acrylics Toner Loaded with 0.5 wt% Silica; Low Shearing Conditions; BET: 300 m^2/g

After blending with low shearing conditions isolated spheres with a diameter up to 100 nm and cluster with diameter up to 300 nm can be seen on the surface. In contrast to prior observation, in the phase shift, the protruded features can not be correlated to harder domains in the phase image. Beside some isolated bright particles, in the phase image only darker spots can be found. The dimension of the dark spots are in the same dimension than the silica particles. One possible interpretation of this effect is, that under low shearing the silylated particles interacts with the surface. This leads to a softening of the contact area. But the adhesion is only small and the particles can easily be removed. PDMS which is not chemically bond to the silica particle remains on the surface leading to soft spheres at the surface.

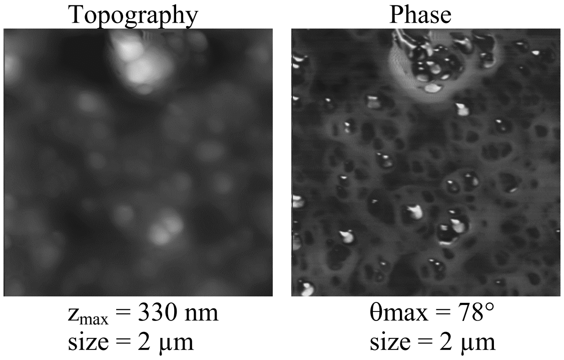


Figure 6a. Topography and phase of polystyrene-acrylic toner loaded with 0.5 wt% silica; low shearing conditions BET: 300m²/g; PDMS treated; WACKER HDK H30TD

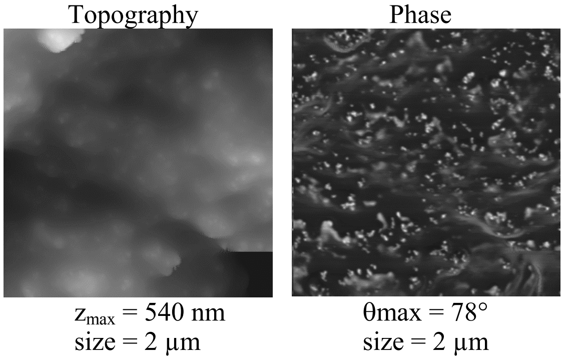


Figure 6b. Topography and phase of polystyrene-acrylic toner loaded with 0.5 wt% silica; high shearing conditions BET: 300 m²/g; PDMS treated; WACKER HDK H30TD

Polystyrene-Acrylics Toner Loaded with 0.5 wt% Silica; High Shearing Conditions; BET: 300 m^2/g

After blending with high shearing conditions, the surface seems to be as smooth as the pure stern-acrylic toner. In the topography no particles can be detect, but in the phase shift they can be detected by a high phase shift. It seems that the particles are squeezed into the surface. The saline-layer of the silica's will interact with the toner surface forming a softer surface area that can be observed by a lower phase shift than the pure resin.

Conclusion

- Pure toner show differences in surface topography from rock-like to spherical depending on the preparation. Phase imaging give a first insight in surface properties. The chemical prepared toner is softer than the other two. Because phase shift is also sensitive to chemical surface properties, the application of complementary experiments using Pulsed Force Mode are necessary. Micro-hardness measurements using Force vs. distance curves are also possible.
- Larger particles show smaller adhesion due to smaller contact area.
- Surface modification by PDMS cause a polymeric surface layer on the silica particles leading to higher adhesion due to softening of the toner surface and increase in contact area.
- Chemical prepared toner show higher interaction than the other resins.
- Low shearing attaches the particles to the surface but high shearing squeezed the particle into the surface.

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Biography

Mario Heinemann received his Ph.D. in Chemistry from the University of Heidelberg, Germany, in 1982.

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