Morphology of Toner-Silica Interfaces

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Abstract

In this study Scanning Force Microscopy (SFM) is used for the investigation of toner particles and toner-silica particle interfaces. The focus is on the simultaneous mapping of topographic features and material properties like local stiffness and adhesion. Topographic images of toner particles of different toner binder compositions were recorded in addition with phase images of hard and soft domains. A series of toner – silica blends were prepared by using a common powder blender. The toner binder resin is styrene acrylics or polyester, respectively. In the topographic images the toner surface is mapped as a rough surface. The mapping of the elastic signals of the silica free toner surface reveals the arrangement of hard and soft domains. With this technique single silica aggregates have been imaged at the toner surface mainly located on topographic rough spots.

Introduction

Fumed silicas are key ingredients in electrophotographic toners and developers. They are widely used as a surface additive for toners and developers. The interaction of silica particles with the toner surface is of high importance for the toner performance.[1-2]
The interactions between toner particles and silica particles are still an open topic of discussion. Atomic Force Microscopy (AFM) has been used as a tool to investigate polymer adhesion forces.[3] Scanning Force Microscopy (SFM) is an effective tool for surface investigations on the nanometer scale.[4-6] The working principle of this type of microscope differs from the conventional microscopes by the way of generating images: A small tip with a radius of about 5 –10 nm mounted on a flexible cantilever beam is scanned over the surface with a constant distance. Typical dimensions of the cantilever are: a width of 20 µm, a length of 100 - 400 µm and a thickness of about 3 µm. Depending on the length and the thickness the force constants of the cantilever can be adjusted between 0.1 N/m to 400 N/m.

For sensitive samples like polymers or resins dynamical techniques like the tapping-mode or pulse force mode were prevailed, were the tip is periodically brought into contact to the surface during the imaging process [5,7,8]. This allows to image soft surfaces without destructive shear forces. In tapping mode a cantilever with a high spring constant is oscillated near its resonant frequency, typically in the range of 100-300 kHz with an amplitude of 30-100 nm. Here, to control the distance between tip and surface a constant damping of the amplitude is used.

In addition, to observing structures on the surfaces the dependency between phase shifts as a function of the free amplitude and the set-point tapping amplitude can be used to investigated mechanical eg. elastic properties of the sample. 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.

Experimental

Raw Materials:

- Toner: monocomponent magnetic; resin: styrene-acrylic; d_{50}=13 µm; T_{soft}=100°C
- Toner: nonmagnetic; color (magenta); resin: polyester-epoxy; d_{50}=12 µm; T_{soft}= 95°C
- Silica: WACKER HDK H2050EP, tribocharge: positive
- Silica WACKER HDK H05TX, WACKER HDK H30TX, tribocharge: negative
- Blending of silica with toner: a low rotating mixer was used; silica loading was 0.4 wt%; mixing time t = 60 min.

For all measurements a commercial stand-alone SFM was used.

SFM Sample Preparation:

Dispersing silica, toner, toner-silica blends on freshly cleaved mica (dry or by ethanol suspensions)

To control the distance between surface and tip a laser beam is focused at the end of the cantilever and the reflected beam is detected in a 4-segment photodiode. A change in sample height causes a change in cantilever deflection. Feedback controlled piezo will readjust the position of the tip to a given height. Recording the piezo movement results in an topography image in the z-axis; combing this with the x-, y-scanning of the cantilever a 3-D image is recorded. In the images differences in height are mapped in different colors where the dark presented low z values and bright areas the high z values.

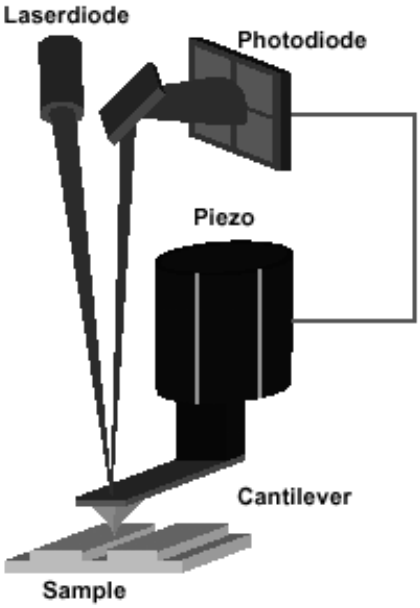


Figure 1. Schematic view of the experimental SFM set-up

Tapping Cantilever: Length: 100 µm; Width: 20 µm;
Thickness: 3 µm; Tip radius: 10 nm;
Resonance frequence: 270 kHz; Damping amplitude: 75 %
Tip: silicon

In tapping mode the phase shift is caused by the fact that the resonance frequency of the free oscillating cantilever and the cantilever tapping the surface are different, Figure 2. The shift in resonance frequency depends on the viscoelastic properties of the sample and of the adhesive force between the sample and the tip. Measuring at a given constant frequency this shift in resonance frequency can be detected as a variation in the corresponding phase, Figure 3.

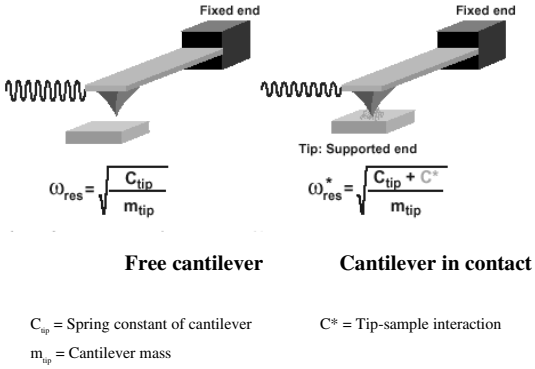


Figure 2. Measuring Surface Properties in Tapping Mode

The shift in resonance frequency is dominated by the elastic modulus of the sample. Thus, a harder material will cause a larger phase shift than a softer one, Fig. 4.

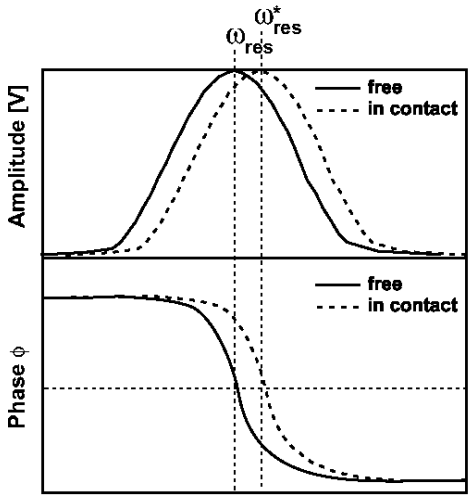
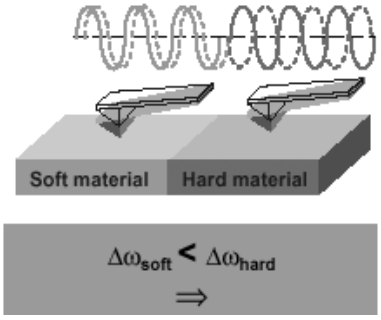


Figure 3. Correlation between frequenca shift and phase shift for the cantilever in and our of contact



Hard materials show larger phase shift

Figure 4. Phase shifts in dependency of material hardness

In the phase images different phase shifts are mapped as different colors: dark areas are the relatively soft materials and bright areas are relatively hard materials.

Results and Discussion

Figure 5 shows the topography (left) and phase shift (right) images of silica free toner surfaces recorded in tapping mode. Binder resin is styreneacrylics; monocomponent magnetic; d_{50}=13 µm; T_{soft}=100°C; crushed type. Obviously, the toner surface is relatively rough in a Z scale of 0.1 – 0.25 µm. Additionally, the phase shift reveals two incompatible phases of different stiffness which we attribute to a hard polystyrene phase (isolated) in a polyalkylmethacrylate matrix (continous).

Contrary to the immiscible blend of polyalkylmethacrylics/polystyrene, where a dispersion of hard polystyrene is observed in a softer continous polyalkylmethacrylics phase, polyester-epoxy resins (nonmagnetic; color / magenta; d_{50}=12 µm; T_{soft}=95°C; crushed type) appears to be a continous. However, similar to the styrene acrylics based toner, the crushed polyester-epoxy resin appears to be rough on its surface, showing edges and surface textures, too.

Toner Surface Morphology

Topography **Phase**

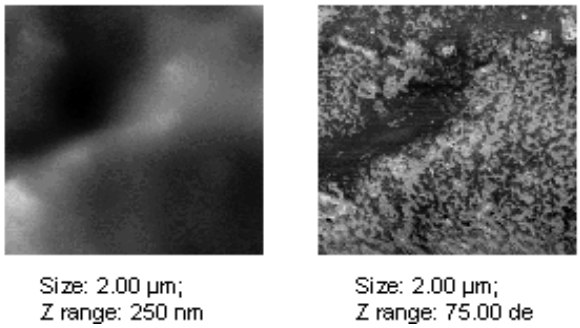


Figure 5. Toner Surface areas with different size and Z ranges

Toner-Silica Surface Morphology

Topography **Phase**

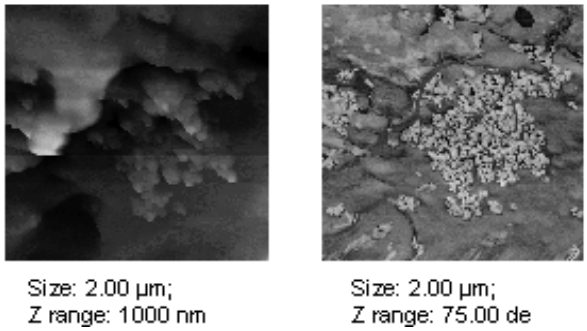


Figure 6. Toner Surface areas with different size and Z ranges

Figure 6 shows the topography (left) and phase shift (right) images of the silica loaded toner surfaces (polystyrene-acrylics + WACKER HDK H2050EP, tribocharge: positive). It turns out that SFM is an effective tool to locate the hard silica particles on the softer polymer matrix. In particular the phase shift images easily distinguish the silica on the toner background. The silica particles seem to adhere with preference at the hot spot ie edges and holes of the toner surfaces. The influence of the silica particle dimension on the surface of the toner particle is still not fully understood.

Further investigations are essential.

Conclusion and Outlook

SFM is an ideal tool to estimate the morphology of toner and toner-silica interfaces. Silica particles are clearly identified due to differences in hardness with respect to the resin. SFM resolves different material properties at the resin surfaces (hard / soft domains) which we relate to polyacrylic and polystyrene domains in case of the styrene acrylics toner. Obviously, silica particles are mainly located at edges and holes at the resin surface (silica loading 0.4wt%). For the polyester-epoxy based toner the investigation has been extended to smaller and larger silica particle sizes. Both silicas, WACKER HDK H05TX and WACKER HDK H30TX, are clearly detected on the resin surface as particles of a more stiff material. Both silicas show aggregates and small agglomerates being more coarse for WACKER HDK H05TX and more finely divided for WACKER HDK H30TX. Both silica tend to adhere on edges and unconformitities of the resin surface.

However with WACKER HDK H30TX the images reveal some penetration of the silica into the resin's surface. This latter effect is not observed for the WACKER HDK H05TX silica.

Further work will be dedicated to the direct measurement at adhesion forces at the nanoscale level.

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Biography

Mario Heinemann received his Ph.D. in Chemistry from the Heidelberg, Germany, University in 1982. In 1984 he joined the research and developing group of Wacker HDK (pyrogenic silica) at Wacker-Chemie GmbH, Germany. His main focus is on the surface silylation of pyrogenic silicas. He actual manage the toner application for WACKER HDK®. He is a member of the IS&T.