Adhesion and Adhesion Distribution in a Model Toner System

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Abstract

In this work, we report the use of a micro-cantilever to measure the rolling resistance of toner particles on a silicon wafer, as a mean to model the Van Waals adhesion between a toner particle and a surface. Results show that there exists a distribution of adhesion in a given toner sample. For a batch of well-blended toner with 100% surface additive coverage, we observe relatively low adhesion with a narrow distribution of adhesion, which is in contrast to the base polymer particle where the adhesion is high and the distribution is broad. For toner with 10% surface area coverage, we observe a very broad distribution of adhesion. The adhesion ranges from high, comparable to the base polymer, to low, comparable to a toner with 100% additive coverage. The results suggest that there is a variation of adhesion on the toner surface for toner with <100% surface area coverage. When the additive covered toner surface is landed on the Si wafer, low adhesion is resulted. When the bare toner surface is landed on the Si wafer, relatively high adhesion is obtained. The use of this rolling resistance technique to determine the distribution of adhesion within a toner sample is discussed.

Introduction

The essence of the xerographic printing process involves generation and development of the latent images on the photoconductor followed by development and transfer of the developed toner particles to paper and fusing. Throughout this process, toner particles are in contact with many surfaces along the printing path, namely from the magnetic brush in the development housing to the photoreceptor to the transfer subsystem and finally to paper. While this printing process has been practiced and commercialized for over half of a century, our understanding of the fundamental aspects of the interactive forces between toner particles and various surfaces are still insufficient. Problem solving has been by intuition and experience. We believe that detailed understanding of the nature of the interactive force, specifically the adhesive forces between toner particles and the surfaces along the print path, is crucial for the development of efficient printing process for high image quality and low run cost printing. Various measurement techniques for toner adhesion have been reported. For instance, Donald and Watson [1] reported the use of an electric field detachment technique to estimate the force requires to "pull off" particles from a magnetic brush (to emulate development) or a photoreceptor (to emulate transfer). This technique only measures electrostatic adhesion force and the adhesion force was estimated based on the field strength and the amount of toner that was detached. Donald and Watson [2] as well as Mastrangelo [3] later demonstrated that toner particles can also be detached from a surface using centrifugal force. This technique is simple and is insensitive to the type of adhesion force (electrostatic versus Van de Waals). Since usually a large number of toner particles are detached in one experimental run, the technique can only determine the average adhesion of many toner particles. More recently Mizes and co-workers [4] and Segeren and team [5] reported the use of atomic force microscopy to determine toner adhesion. In this case, a toner particle is glued onto the tip of an AFM micro-cantilever. Since the force constant of the cantilever can be calibrated, the adhesion force between the "glued" toner particle and the surface can then be determined on the AFM accurately and easily. This method, however, can only measure the adhesion of one designated area within a toner particle in a given measurement. For a given toner sample, there exists thousand of toner particles and the distribution of size and shape will depend on the manufacturing method. Given that, should one expect the existence of a distribution of adhesion too? After all, toner charge is known to have a distribution and can be determined by the charge spectrograph technique.

In 2007, Ding and co-workers [6] reported the determination of the van de Waals adhesion between polystyrene latex microspheres on silicon substrates using the rolling resistance measurement technique with a nano-manipulator inside the vacuum chamber of a SEM. This experimental set-up was later modified such that the rolling resistance of spherical emulsion-aggregated polymer particles on silicon wafer can be measured in lab ambient [7]. In this new apparatus, the rotation or displacement of polymer particles was captured by a high speed, high resolution camera. Here, we report the use of the rolling resistance technique to determine the adhesion of model toner samples of varying amount of silica surface additives, from 0% (base particle) to 100% theoretical surface area coverage (SAC). By determining the rolling resistance of multiple toner particles in a given sample, we are able to show that there exists a distribution of van de Waals adhesion in the toner samples. For the sample with 100% SAC, the work of adhesion is low and the distribution is narrow. On the other hand, the work of adhesion becomes very broad, from low to very high, for the 10% SAC sample. The result is discussed in term of the additive-spacer-effect model. Low adhesion is resulted when the toner is landed with the additive separating the toner surface and the substrate. The overall results suggest that, (1) surface additive reduces toner adhesion due to the additive spacer effect, (2) like toner charge, there exists a distribution of adhesion in a given toner sample; and (3) adhesion on the toner surface is not uniform when the surface area coverage is low.

Experimental

Materials and Measurement Apparatus. The toner materials studied in this work were synthesized in house using the emulsion-aggregation technique. The additive used in this work was silica R812 from Degussa. Description of the rolling resistance apparatus and the measurement procedure have been documented in earlier reports [6,7].

Results and Discussion

Rolling Resistance Measurement

The apparatus used for the roll resistance measurement has been described earlier [7]. Figure 1 depicts a measuring sample consist of polymer particles randomly "dusted" onto the silicon substrate. The wafer is mounted on a nano manipulator and can be moved in the x-y-z direction in very small steps. At the start of the measurement, the toner particle is brought to the close proximity of the AFM cantilever by the nano-manipulator and a close up view of the toner particle and the cantilever is shown in the inset of Figure 1.

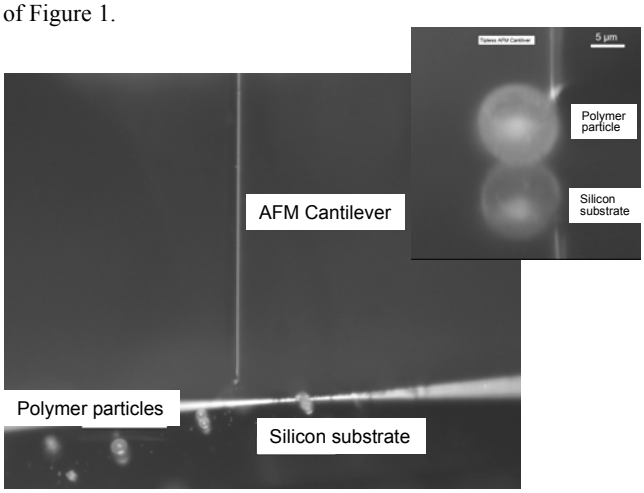
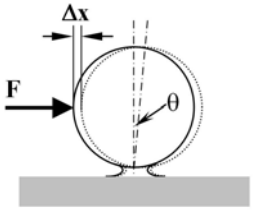


Figure 1. Experiment set up for the rolling resistance measurement showing polymer particles on a Silicon wafer relative to the cantilever (inset: a close up view of a polymer particle)

As the wafer is moving from left to right (inset in Figure 1), this will result in a pushing force towards the polymer particle. The rolling resistance moment (M) of a particle on a flat substrate is given by:



$$M \approx 6\pi W_A (D/2)^2 \theta$$

where W_A is the work of adhesion; D is particle diameter; and θ is the angle of rotation.

Experimentally, $M \approx F \times (D/2)$ and $\theta \approx \Delta x/(D/2)$, the slope of the force displacement curve is given by:

$$k = \frac{F}{\Delta x} \approx \frac{2M/D}{\theta D/2} = \frac{4M}{\theta D^2}$$

Then $M \approx \frac{kD^2}{4}\theta$ and $\boxed{W_A \approx k/(6\pi)}$

By analyzing the initial slope of the force displacement curve, the work of adhesion (W_A) is determined.

Adhesion of Model Toner Particles

A series of spherical model toners were prepared by blending the based toner particles (~ 6 μm) with a 12 nm hydrophobic silica additive at various surface area coverages, from 0% (base particle) to 100%. SEM micrographs of these toner particles are given in Figure 2.

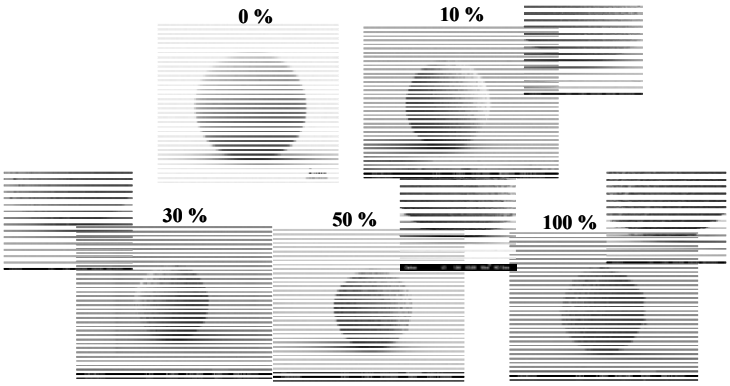


Figure 2 SEM micrographs of toner particles with varying amount of silica additives (from 0% to 100% surface area coverage).

These toner particles were then dusted onto the silicon wafer randomly and their adhesions with the silicon surface were determined by the rolling resistance technique. Typical displacement force curves are given in Figure 3.

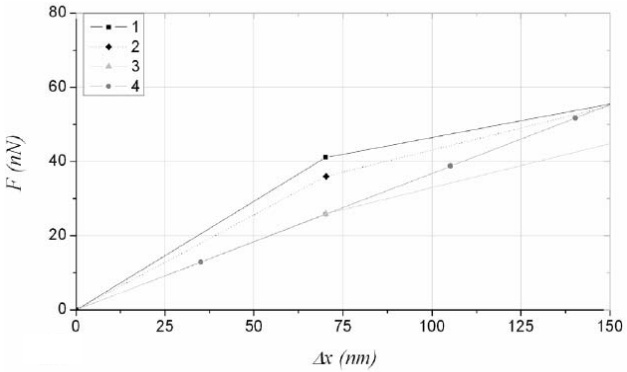


Figure 3. Typical force displacement curves for the roll resistance measurement.

During our initial scoping experiments, we found that there was a wide variation of W_A, especially for samples with low SAC. To ensure that we are observing variation with statistical significance, we have been carefully performing 10-20 independent measurements for each sample. The histogram of W_A is plotted in Figure 4. The results show that there exists of a distribution of adhesion even for the base particle with W_A varies from ~ 10 to 40 mJ/m^2. Toner adhesion reduces sharply to ~ 6 mJ/m^2 with a very narrow adhesion distribution for toner with 100% SAC. The low

adhesion is attributable to the separation of the toner surface from the silicon surface due to the additive spacer. Since the toner surface is fully covered, the variation of adhesion is small, resulting in the narrow adhesion distribution. As the SAC decreases, the distribution of the adhesion becomes very broad, ranging from low adhesion comparable to the 100% SAC toner to high adhesion comparable to the base polymer particle.

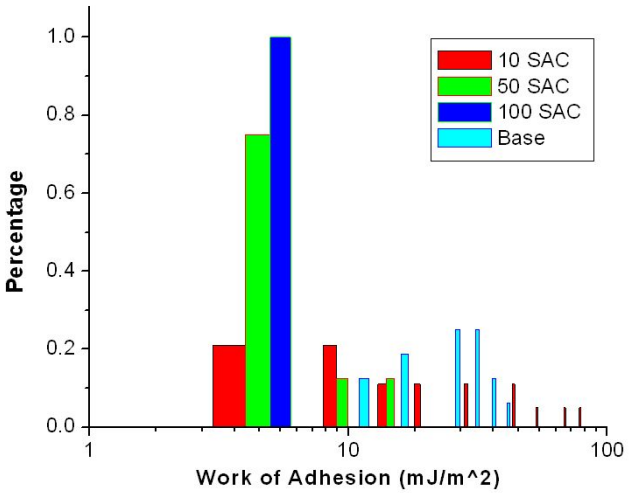
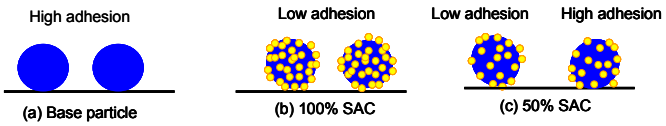


Figure 4. Histogram of work of adhesion for model toners with different SAC.

Interpretative Model for the Adhesion Data

A model to rationalize the overall result is given in Scheme 1. We suggest that, for toner with 100% surface additive coverage, the entire toner surface is covered with silica additive. The toner adhesion is low because there is an additive spacer separating the toner and the silicon surface. Since the entire toner surface is covered by additive, the variation of adhesion is small, and a narrow distribution of adhesion is resulted.

Scheme 1.



According to our experimental procedure, toner particles should be randomly landed onto the silicon surface. At 50% SAC, a significant amount of the toner surface is still covered with additive (Figure 2). When these particles are landed on the silicon surface, low adhesion should observe because of the additive spacer effect. Indeed, a significant amount of toner with 50% SAC exhibits very low adhesion analogously to the 100% SAC toner. In addition, there also exist toner surfaces that are bare or partially covered with additives. This should result in higher adhesion. In fact, the histogram shows that indeed the adhesion distribution for the 50% SAC toner is broader.

The adhesion distribution becomes very obvious for the 10% SAC toner. The result indicates that due to the insufficient surface additive coverage, the toner surface is in a wide range additive coverage state, from bare surface with no additive to patches with full additive coverage. Indeed, experimentally, we observe a wide range of adhesion, from ~ 4 mJ/m^2 comparable to the 100% SAC toner to very high adhesion (50 – 80 mJ/m^2) comparable to the bare toner particle.

Concluding Remarks

This work demonstrates that for the first time there exists distribution of adhesion in a given toner sample. This should not come too surprising as the existence of charge distribution in toner is well known. This work also demonstrates that distribution of adhesion can be acquired by multiple rolling resistance measurements from a given toner sample and suggest that rolling resistance may be a useful quality control tool for toner manufacturing. Although toner formulation is often very complex and consists of multiple additives, their performance is always optimized with optimal flow where the adhesion would be low and uniform. Any error in toner manufacturing (human or machine) would result in non-uniform additive distribution and should be detectable by the rolling resistance technique described in this work.

It is important to note that in the current set up, only van de Waals adhesion between toner particles and the silicon surface is measured. We recognize that adhesion originates from electrostatic force is an important component of xerography. Work is continuing to modify the experimental set up and procedure so that electrostatic adhesion can be determined analogously.

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Author Biography

Kock-Yee Law received his BS in chemistry from The Chinese University of Hong Kong (1974) and his PhD in photo-organic chemistry from The University of Western Ontario (1978). He has been at Xerox Webster for over 28 years and he is currently a technical manager in the Xerox Innovation Group responsible for the development and delivery of Nanotechnology for the future.

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