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Adhesion properties of nanoparticle-coated emulsion aggregation toner

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ABSTRACT

Toner is the key material in printing and copying processes. Fundamental understanding of toner detachment and adhesion during the printing process is critical to improve both the efficiency of toner usage and the quality of print. To control their adhesion property, toner particles can be surface-coated with nanoparticle additives to modify their surface roughness, and consequently, to tune their adhesion properties. In this study, a technique based on the rolling resistance moment of the particle–substrate adhesion bond is used to quantify the effect of nanoparticle surface area coverage (SAC) on the effective work of adhesion of individual toner particles. Nanoparticle-coated model emulsion aggregation (EA) toner microparticles with the specified SAC levels of 0%, 10%, 50% and 100% were studied and the corresponding particle–substrate work of adhesion values were determined and compared. It is quantitatively demonstrated that the work of adhesion between a surface-coated toner particle and a flat silicon substrate decreases significantly with increasing nanoparticle SAC, which provides an effective means to tailor the adhesion performance of the EA toner. Also, based on the experimental data, for a nanoparticle-coated microparticle on a flat substrate, two possible modes of contact formation were identified and discussed.

1. Introduction

In electrophotographic printing, charged micro-sized toner particles are transferred from the magnetic brush inside a toner cartridge to the photoreceptor drum, then from there to the transfer belt, and finally to the paper for fusing and binding. Fundamental understanding of toner detachment and adhesion during the printing process is, therefore, critical to improve both the toner usage efficiency and the print quality. Due to the technological significance, using various techniques, the adhesion of micro-scale particles has been studied extensively and reported in the literature [1–12]. Electrical field and centrifugal force detachment methods have been two of the popular techniques [1,2,4,5,7,8,11]. The former technique emulates detachment of charged toner particles from the magnetic brush to the photoreceptor and from the photoreceptor to paper. Under the specified experimental conditions, toner particles detach when the applied detachment force exceeds the particle–substrate adhesion force. Statistical adhesion data is obtained by analyzing the amount of toner detached as a function of the electric field. However, adhesion originating from both electrostatic and non-electrostatic forces are operating, and, thus, such measurements provide only limited insight for the type of adhesion force that is dominant in the detachment process. The same shortfall also exists for the centrifugal force detachment technique as well as the recently-proposed vibration assisted detachment technique [13]. The use of a calibrated atomic force microscope (AFM) cantilever to directly measure the adhesion force between a toner particle and a substrate represents a significant advance in toner adhesion measurement [1,6,14,15]. The adhesion force is measured directly since the force constant of the cantilever can be calibrated accurately. However, since the measurement process involves physically fixing (*e.g.*, gluing) a toner particle onto the end of the cantilever, each measurement can only determine the adhesion of one area of a toner particle in single measurement. Therefore, the "cantilever measurement" does not represent an average adhesion of a toner particle, nor does it provide any statistical information regarding the adhesion of the toner sample. In view of this backdrop, Lee [16] in his 2008 letter to the editor of the Journal of Imaging Science and Technology discussed the existence of discrepancies in the literature and the inaccuracy of these earlier adhesion data in detail. Part of the difficulty in the adhesion characterization of toner is the lack of qualified adhesion measurement techniques that can be used to convincingly characterize and differentiate the electrostatic and non-electrostatic components of the adhesion force. Another complication in qualifying the experimental data has been the type of toner samples being studied and the techniques used to prepare the toner samples. For example, while in earlier works irregular conventional toners were used, in recent studies spherical chemical toners are employed more often. Furthermore, the type of additives and the "aging" of the toner samples and associated complications were seldom systematically studied and/or reported

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in earlier works. These factors complicate the comparison and interpretation of available adhesion and detachment data. Considering these experimental issues and accompanying modeling difficulties, the existence of the current controversy as to the nature of the force components in adhesion should be no surprise.

The particle–substrate adhesion has been theoretically investigated since early 70s. Several contact mechanics-based adhesion models have been developed, such as the Hertz model, JKR (Johnson, Kendall and Robert) model [17], DMT (Derjaguin, Muller and Toporov) model [18] and MD (Maugis and Dugdale) mode [19]. Later, Johnson and Greenwood [20] proposed a unifying framework for existing models, and established the transition between these theories and their applicability zones for ranges of external loads and an elasticity parameter. The adhesion models and experimental techniques discussed above all focus on the one-dimensional (axial) adhesion and assume a symmetric pressure field at the particle–substrate contact. Recently, two-dimensional adhesion model has been proposed to analyze the rolling motion of an adhered particle, where the stress distribution at the particle–substrate contact becomes asymmetric during pre-rolling and rolling. For example, adhesion and frictional forces between micro-spherical particles were studied by Heim and Blum [21] on the basis of rolling resistance moment using an AFM. The rolling resistance moment is generated by the adhesion bond between the particle and substrate against the rolling motion of the particle, which can be estimated based on the adhesion model of Dominik and Tielens [22]. Recently, Cetinkaya and co-workers experimentally confirmed the existence of the rolling resistance moment of an adhered polystyrene latex (PSL) microsphere with a non-contact acoustic excitation technique [23,24].

In this work, we report the use of a recently developed rolling resistance moment technique [25,26] in determining the adhesion between model emulsion aggregation (EA) base and surface-coated toner particles and silicon substrate to quantify the effect of nanoparticle coating on the adhesion properties of these toner particles. A lateral force acting on a spherical particle in obtaining a detachment criterion has been used to predict the initiation of rolling-based detachment of the particle. This technique was previously used to investigate the adhesion between the PSL microspheres and silicon substrate in the vacuum chamber of a scanning electron microscope (SEM) [26]. In current study, the technique is employed to characterize the adhesion properties of the toner particles in the ambient under an inverted optical microscope. While the spatial resolution of the optical microscope is substantially inferior to that of the SEM, performing measurements in the ambient can avoid the possible sources of inaccuracies associated with the charging of the nonconductive toner particles by the SEM electron beam. Moreover, working in the ambient provides the flexibility to explore the effects of certain realistic operational parameters such as the temperature and humidity on particle–substrate adhesion, which is important for toner adhesion characterization but difficult to achieve in high vacuum. Since the base toner particles are randomly “dusted” (dry-deposited) onto the silicon substrate and the silicon substrate is doped to be electrically conductive, no toner charging is anticipated in the experiments, and the adhesion forces measured in the reported experiments should be purely van der Waals in nature. In addition, in order to determine the distribution of the adhesion properties, multiple rolling resistance moment measurements on the base toner particles have been performed.

It is known that the surface roughness of the particle has a significant effect on the particle–substrate adhesion [2,4,6]. In recent decades, the influence of surface roughness on particle–substrate adhesion has attracted considerable attention, and several adhesion models have been proposed for taking the surface roughness of the particle and/or substrate into account to better predict the particle–substrate adhesion [27–30]. Generally, for a particle with a rough surface settled on a flat substrate, the contact area between the particle and the substrate is much smaller than that between a smooth particle of the same diameter and the substrate. Therefore, in general significant reduction in the adhesion force is expected with increasing particle surface roughness. In this work, the effect of additive nanoparticle coating on the toner adhesion has been systematically explored by measuring the adhesion of a series of micron-scale model toner particles surface-coated with silica nanoparticle additive at various surface area coverage (SAC) levels.

2. Materials

To examine the effect of additive coating on toner adhesion, a series of model toners of 6.0 μm nominal diameters were surface-coated with fumed silica nanoparticles (R805, Degussa AG, Frankfurt, Germany) at various specified SAC levels, namely 10%, 50%, and 100%. The SEM images of such surface-coated near-spherical model coated toner particles are shown in Fig. 1. The outer layer of the base toner particle consists of a polyester resin, cyan pigment and wax. The nominal size of the silica nanoparticle is about 12 nm in diameter, but the nanoparticles occasionally can form aggregates as large as 100 nm in effective diameter (Fig. 1). The model toner particles employed in the experiments were prepared by the EA process [31], and, subsequently, surface-coated with silica nanoparticles using a toner blender at the Xerox Research Center (Webster, New York, USA). The toner particles were used in the reported experiments as-received with no additional aging and/or chemical treatment and were dry-deposited on a plasma cleaned single-crystal silicon (p-type doped (100) oriented) substrate immediately prior to the pushing experiments.

3. Experimental setup

The schematic of the rolling resistance moment-based lateral pushing experimental setup is depicted in Fig. 2. When a lateral pushing force is applied to an adhered particle, the stress distribution in the particle–substrate contact area becomes non-uniform, which creates a moment (rolling resistance moment) to resist the free rolling motion of the particle. This rolling resistance moment is proportional to the angle of rotation of the particle [23,25]. With increasing lateral force, eventually the rolling resistance moment is unable to withstand the external rolling moment, and the particle begins rolling (at early stages, almost certainly without slip) on the substrate surface.

The experimental setup developed for the reported work is composed of two opposing *xyz* linear positioning stages (122-1135/1155, OptoSigma Inc., Santa Ana, California, USA) mounted on the top of an inverted optical microscope (Epiphot 200, Nikon, Japan). These positioning stages are driven by six piezoelectric actuators (MRA 8351, New Focus, Inc., San Jose, California, USA) that can provide linear motion with a displacement resolution of approximately 30 nm. A piezoelectric bender (CMBP 05, Noliac A/S, Denmark) that provides fine positioning at a sub-nanometer resolution is mounted on one of the axes of the *xyz*-linear stage. The positioning and particle pushing processes can be monitored through a 100× objective lens using a high-resolution digital camera (DXM 1200, Nikon, Japan) attached to the optical microscope. For pushing tests, a tipless AFM cantilever with a length of 350 μm and a nominal force constant of 0.03 N/m (CSC 12, MikroMasch, Inc., Wilsonville, Oregon, USA) was attached to the free end of the piezoelectric bender, and the silicon substrate with toner particles deposited was mounted on the opposing linear positioning stage (Fig. 3).

During the lateral pushing test, a *dc* voltage was applied to the piezoelectric bender to actuate the bender. The tipless AFM cantilever that attached to the free-end of the piezoelectric bender was thus actuated to push a chosen particle adhered on the substrate. The *dc* voltage was increased in discrete steps, and the corresponding lateral pushing force was thus also increased discretely. By acquiring a series of digital images, the entire pushing test was recorded with a time interval of approximately 30 s per each pushing step (for image