Measuring Work of Adhesion of Polystyrene Microspheres

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Introduction

Particle adhesion is relevant in fields ranging from aerospace and energy to civil engineering and medicine. The functions of aerodynamic surfaces, heat exchangers, solar panels, ventilation systems, and blood vessels are affected by the buildup of particulates on their surfaces. Direct measurement of the adhesive force between a particle and a surface is key to understanding and mitigating particle fouling. Approaches such as the Johnson-Kendall-Roberts (JKR) and Derjaguin-Muller-Toporov (DMT) models offer a first approximation of the forces involved but do not account for non-idealities like roughness or plastic deformation. Experimental measurements of adhesive forces often deviate significantly from predictions[1].

One approach to measure adhesion is the colloidal probe technique, which uses a particle attached to the tip of an atomic force microscope (AFM) cantilever. The particle is touched to a surface and then withdrawn and a pull-off force (F_{PO}) determined by cantilever deflection. F_{PO} can be used to estimate work of adhesion (W_a) and other properties from existing models[1]. We describe a new method for producing colloidal probes using wax as an adhesive to attach micrometer-scale spheres to AFM tips. This method can be used with a range of particles and minimizes the potential for changes to the particle surface chemistry or geometry from exposure to heat, chemicals, radiation, or external forces. Particle attachment to AFM tips is robust and reversible, allowing old particles to be replaced with new ones in a few minutes. Pull-off measurements using polystyrene (PS) particles, pristine and modified with myristyltrimethylammonium bromide (14-TAB), were collected from various substrates to demonstrate the viability of this technique and investigate the impact of particle surface modification.

Experimental

Materials: Mounting Wax 80 (MW80) from Electron Microscopy Sciences was used as received. The reported flow point is 80°C. Differential scanning calorimetry (DSC) measurements carried out in a Q20 DSC (TA Instruments) found a glass-transition temperature (T_g) of 32°C. Mechanical analysis of MW80 samples was carried out with an RSA-G2 Solids Analyzer (TA instruments). Results showed time independent moduli with an average storage modulus of 1.73 GPa and average loss modulus of 170 MPa, corresponding to a rigid solid. MW80 films were spin-coated from ethanol onto glass slides.

PS microspheres, 0.7-2 µm in diameter, were prepared by soap-free emulsion polymerization at 70°C[2]. Particle sizes were characterized with a Zetasizer Nano (Malvern Instruments). Particles were cleaned by centrifuging and resuspending in 16 MΩ deionized water three times. Particles of this type have a highly negative surface charge due to sulfate groups derived from the radical initiator[3]. Modification of anionic surface groups with cationic alkylammonium surfactants (14-TAB from Fisher Scientific) was carried out in water with the modified particles cleaned in water by centrifuging and resuspending three times. Cleaned particles were dried under vacuum at 60°C for 24 hours and stored under nitrogen at room temperature. PS standards (molecular weight of 290 kDa and 170 kDa, Pressure Chemical) were spin-coated onto silicon wafers from toluene. The presence of PS films was confirmed by contact-angle measurements.

Probe Fabrication: The probe fabrication apparatus had two parts, the *Probe Mount* and the *Material Mount*. The Probe Mount was built around a 3D-printed plastic body and head shown in **Fig. 1**. A ProJet® 3500 HDMax printer was used to produce 3D-printed components out of proprietary polyurethanes (Visijet®). **Figs. 1a**, **b,** and **d** show the plastic head from top, side, and bottom views. The flat body in **Fig. 1e** was mounted on an Olympus BX-60 microscope stage via slots in the back and the head attached to the body with a set of pegs as shown. A cross section of the head with fittings is shown in **Fig. 1c**. Solid gray indicates plastic that had been cut off by the viewing plane. A 0.17 mm thick plate glass sheet (5) was bonded with epoxy (Loctite® clear, quick-set) on the top of the head, covering the rectangular slot in the front to create a groove that fit an AFM chip (6). The chip was held from below by a Teflon™ tongue (4). A steel tongue (3) supported the Teflon™. Wires (not shown) connected a Tenma DC power supply to a copper pin (8) at each end of the heating element (7, only one end shown). The heating element was a 0.12 mm diameter Chromel™ wire and was passed over the Teflon™ tongue to ensure good contact with the AFM chip. The Teflon™ tongue was raised to clamp a chip in place using the clamping screw (1) and nut (2). A hinge (9) allowed the front of the head to be tilted up to 90°.

The Material Mount used a 3D-printed bracket with a slot on one end that held standard coverslips. The bracket

was bolted to a 3-axis translation stage. The stage was bolted to an aluminum plate clamped onto the table next to the microscope. A coverslip held in the bracket could be manipulated under a microscope independently of the microscope stage. The thin profile of the setup meant it could be used without long working distance optics, even for 100x objectives.

To make a colloidal probe, an AFM chip was loaded in the Probe Mount with the tip pointing up. The tip apex could be ground down to produce a larger surface for mounting particles. Tips flattened in this way are shown in **Fig. 2**. The Probe Mount was attached to the microscope stage. MW80 was melted on a hot plate and a few milligrams of the wax were spread on a coverslip with a pipette tip. These wax-coated coverslips could be reused indefinitely. The coverslip was loaded into the Material Mount with the wax side facing down and positioned above the AFM tip. The AFM tip was heated by running a constant electrical current through the heating element. The microscope stage was raised to bring the hot tip into contact with the wax, then withdrawn. The presence of wax on a tip could be verified optically due to thin film interference. **Figs. 2a, b,** and **c** show the ends of flattened-apex AFM tips without wax, with wax, and with wax and a 2 μm particle. Once wax was transferred to the tip, the heating element was turned off and the wax-coated coverslip replaced with a coverslip bearing particles. This coverslip was prepared by blowing dry particles out of a glass pipette onto the coverslip. The coverslip was positioned particle-side down under the microscope. The AFM tip was aligned under a particle and raised to briefly contact the particle. Particles transferred between the glass and AFM tip readily, often "hopping" from glass to tip and back. When a particle had been transferred to the desired location on the tip, the tip was heated again to soften the wax and fix the particle in place. **Fig. 2d** shows a flattened conical tip and attached particle. Particles could be removed by pressing a heated tip onto wax.

Probe fabrication was conducted below the T_g of PS (100°C) to minimize potential PS chain rearrangements. The heating sequence was determined experimentally for each heating element to use the minimum amount of heat needed to fasten the particle to the tip. AFM tip temperatures were monitored using micrometer-sized crystals of materials with known melting points, such as vanillin (melting point 81-83°C, Sigma-Aldrich). A crystal was placed on an AFM tip and observed during heating to check for melting. This method ensured that the heating sequences used did not exceed 90°C.

Wax/Particle Interactions: Several approaches were used to test if PS particle surfaces could be contaminated with MW80. Colloidal probes were imaged with a Verios Scanning Electron Microscope (SEM) to determine the morphology of the particle/wax interface. PS particles embedded in wax were prepared by placing a droplet of PS/water suspension (10 wt% PS) onto glass slides spin-coated with MW80. After drying for 24 hours, the slides were heated on a hotplate at 70-85°C for 1-6 minutes. Loose particles were removed by ultrasonication in water. Samples were imaged using an MFP-3D AFM (Asylum Research) in AC mode. Contact angle samples of wax droplets on PS films were prepared by melting 3-8 mg chips of wax onto PS films on a hotplate at 85°C for 2 hours.

Probe Testing: Pull-off measurements were conducted with the MFP-3D AFM using a variety of particles on PS, glass, silicon, and other substrates. Unmodified tips, tips bearing rigid 1μm silica particles, and tips coated with wax were also tested to identify possible viscoelastic contributions from the wax to pull-off measurements. The spring constant (k) of each tip was determined using the thermal tuning method. Typical k values were 1-3 N/m, but some probes had k ~40 N/m. Pull-off curves were collected singly or in grids to create force maps. The largest force maps collected were 40 μm per side with 42 lines of 42 points. Tip approach velocities between 100 nm/s and 4 μm/s were tested with a velocity of 1.98 μm/s being found to give reliable resolution while minimizing the time particles spent in contact with the surface outside of the set dwell time. Most measurements used zero dwell time, but times up to 1s were tested. The force exerted on the substrate before probe retraction was varied from 0.5 to 200 nN. A force of 2 nN was selected for most measurements as the smallest force that was reliably detectable. F_{PO} was calculated from force curves using IgorPro software.

Results and Discussion

Wax/Particle Interactions: Wax droplets on PS showed wide variations in contact angle due to irregular droplet perimeters, but in all cases contact angles were greater than 90° indicating that liquid MW80 did not readily wet PS. In SEM images of probe tips, no meniscus between particle and wax was visible. Instead, the wax appeared to dimple under the particle, even when the particle was pressed with enough force to flatten it. The extent of these deformations was most evident when a stiff cantilever was used to push the particle into heated wax, as shown in **Fig. 3a**.

Dried from suspension, PS particles formed self-assemble monolayers (SAMs) as shown in the AFM image in **Fig. 3b**. At long heating times, wax appeared to creep into SAM interstices with particles having sunk into the wax. **Fig. 3c** shows a sunken SAM where some particles were dislodged during cleaning. At the longest heating time, it appeared that particles sank so deep that wax seeped up between the holes in the SAM. **Fig. 3d** is an AFM phase retrace overlaid on a height retrace and shows PS particles (yellow) mostly engulfed by the risen wax (purple). Even so, a sharp transition where the particle met the wax was evident. The high contact angles measured for MW80 on PS and the observations from AFM and SEM images suggest that MW80 does not creep onto PS surfaces during probe fabrication.

Pull-off tests with bare tips, wax covered tips, and tips with a silica particle attached, did not detect any deformation of wax that might complicate measurements of particles subject to viscoelastic deformation. Force maps on PS substrates using 1.95 μm particles of pristine and 14-TAB

PS are shown in **Figs. 4a** and **b**, respectively. F_{PO} drift, probably due to plastic deformation of the particle, was observed in some tests and can be seen in **Fig. 4c** (same data as Fig. **4b**). Evidence of surface asperities changing F_{PO} encountered during some tests was typically observed as a decrease in F_{PO} by up to 2 orders of magnitude. Suspected sources of asperities include dust contamination and particle deformation during pull-off. The effect of surface asperities could be reduced by increasing particle dwell time on the substrate at the risk of increased plastic deformation. Measurements from these tests showed that the tip deflection would decrease by several nm while the particle was held on the surface. This was followed by a return to the initial F_{PO} range suggesting that asperities were deformed or deflected to improve particle/substrate contact[4]. The influence of surface asperities and plastic deformation means that further work is required to fully characterize particle/surface interactions.

Conclusions

Characterization of MW80 and PS films and particles indicated that the described fabrication system can produce rigidly attached PS colloidal probes without contaminating particle surfaces with adhesive (wax). Differences in F_{PO} were observed between the functionalized and bare PS particles, but variation within the data prevents specific conclusions at this time. Planned methods for improving data quality include better dust control and modified substrate preparation. Pull-off measurements using over 30 colloidal probes have demonstrated the viability of such probes for measuring adhesion and established a foundation for future studies.

References

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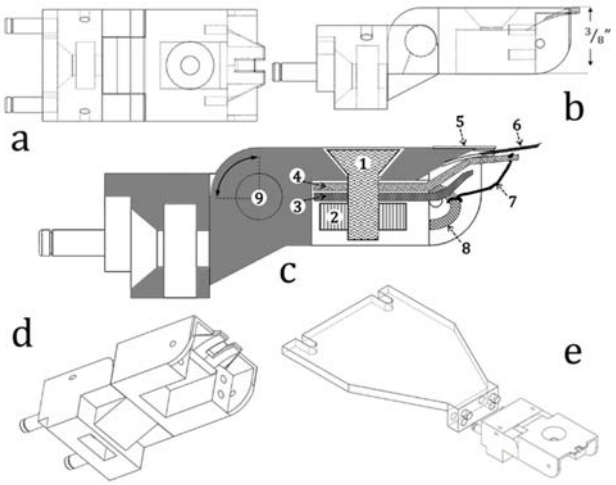

Figure 1. Probe Mount for colloidal probe fabrication.

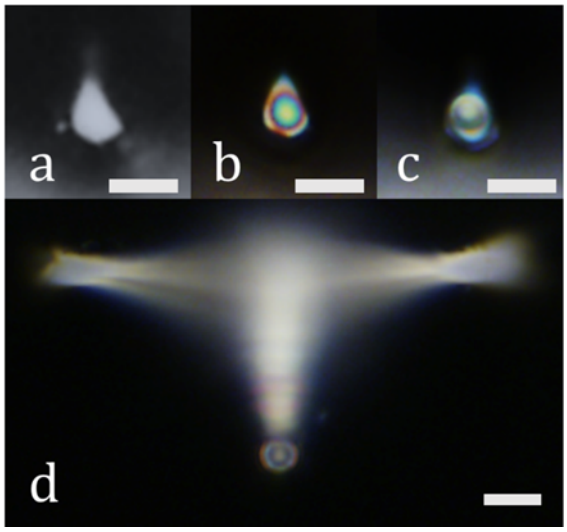

Figure 2. Optical microscope images of flat-ended AFM tips. Tips (a-c) point out from the page. Tip (d) points downwards. Scale bars are 5 µm.

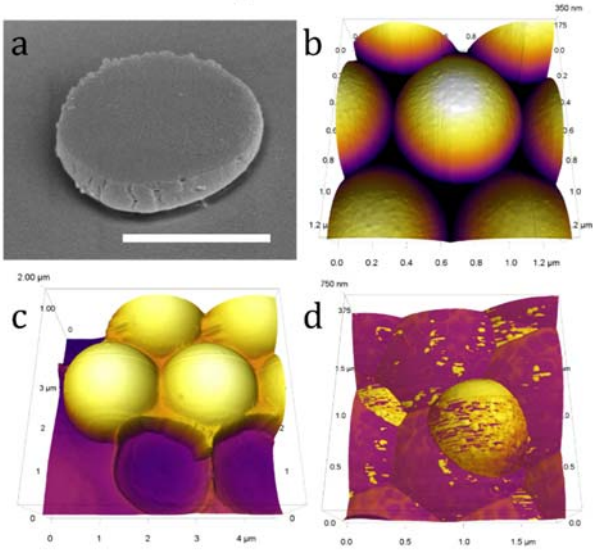

Figure 3. SEM and AFM images of PS particles on MW80. Scale bar in (a) is 1 µm.

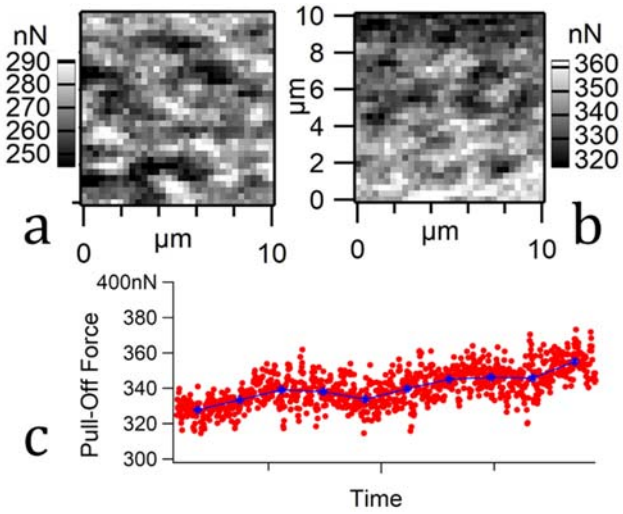

Figure 4. AFM measurements of pull-off force.