

The Relationship between nanoscale AFM adhesive force measurements using calcite crystals with macroscale contact angle and scaling characteristics.

R. D. Boyd^{1*}, S. Bargir¹, S. Dunn², B. Jefferson¹

¹School of Water Sciences, Cranfield University, Cranfield University, Bedfordshire, MK43 0AL, United Kingdom, *r.d.boyd@cranfield.ac.uk

²Nanotechnology Department, Cranfield University, Cranfield University, Bedfordshire, MK43 0AL, United Kingdom

ABSTRACT

The strength of calcite adhesion to various surfaces was measured using atomic force microscopy. This nanoscale measurement was compared to both macroscale work of adhesion, as determined by contact angle measurements, and the rate of scale formation, calcite being the major component. A broad correlation is seen in both cases. Possible causes of deviation between adhesion measurements and the macroscale observations include affect of and impurities in the measuring media. Also distribution of adhesion forces played an important role when comparing adhesion forces with scaling measurements.

1. INTRODUCTION

The atomic force microscope has been widely used to perform force measurements with manometer precision and piconewton sensitivity[1]. A standard probe with a silicon or silicon nitride tip has been used to obtain the adhesive properties of materials ranging from metals and plastics[2] to biofilms [3;4]. However by attaching specific particles to the end of AFM cantilevers then actual adhesive forces can be measured. This technique has been used to measure the adhesive forces of colloidal particles[5-8], fungi spores[9-12] and bacteria[13]. Although little work has been conducted into how these nanoscale measurements relate to macroscale properties. Examples of such studies include bacterial adhesion[14;15] and in the comparison of immunological techniques [16].

Here a comparison is made between nanoscale force measurements taken with a tip modified with a calcium carbonate (calcite) crystal with real macroscopic scaling and contact angle measurements. Two methods have been employed to modify the probe. The first is to grow the crystal on the AFM tip and the second is to attach a crystal directly onto the probe using an adhesive.

Contact angle measurements are a well established method to determine a surface's energy. From which a theoretical adhesion force between to surfaces so long as both surface energy parameters are known.[17] Scale formation is a major problem in the water industry. A layer of scale can reduce the

efficiency of a water heating system by up to 95 % [18]. Although the exact mechanism of scale formation is not fully understood it is known that it is initiated by the adhesion between calcite crystals and surfaces. Clearly the adhesive strength of calcite crystals must be related to the scaling properties.

2. EXPERIMENTAL

2.1 Materials

Nine materials were selected with varying surface compositions and topographies. Two samples each of stainless steel (mirror-finished – MF steel and roughened steel –R steel) and gold (0.1 mm and 0.3 mm thick layers deposited onto glass) plus aluminium, polytetrafluoroethylene (PTFE), titanium nitride (TiN), and two diamond-like-carbon-graphite surfaces; DLC-graphite and Dymon.. All materials were provided by a Teercoatings (Droitwich, Worcestershire, UK).

2.2 Contact Angle Measurements

Contact angle measurements were taken using the sessile drop method. The liquids ultra-pure water, 1-bromonaphthalene (BRMN), formamide (F) and Ethylene glycol (EG) were used and the surface energy parameters are given in table I [19;20]. A 10 µl drop of each liquid was dispensed and allowed to come into equilibrium Images of the drop were taken using a Jai-CV-M90 Interlaced CCD camera and contact angle measurements were taken from both sides of the drop using Image Pro Plus software. This was repeated eight times for each surface. From this data the surface energy components and a theoretical adhesive force to calcite crystals could be determined using the approach given in [21].

2.3 Production of Modified AFM Probes

Calcite grown probes are prepared as follows: First the cantilever (Pointprobe plus, PPP-CONT-50) was cleaned with 0.1M HCl acid for minutes. A droplet of 0.1 M Na₂CO₃ was dispensed on a petri dish followed by the same volume of 0.1 M CaCl₂ inducing the formation of CaCO₃ precipitate. A quarter of the length of the cantilever was inserted into the supersaturated droplet and was left in

solution for 1hour. The process of introducing the cantilever into a supersaturated solution was repeated until a calcite crystal of a sufficient size was produced,.

Attached probes were prepared as follows: A drop of cyanoacrylate adhesive (Pacer technology) was deposited using a freshly prepared glass probe prepared using a flass puller (PC-10, Narishige Co. Ltd, Tokyo, Japan) with the aid of an MMO-202ND Three-axis Hanging Joystick Oil Hydraulic micromanipulator (Saitama, Japan), after which a calcite crystal is attached onto the end of the cantilever micromanipulator. The crystal is positioned in the desired orientation for about 10-15 seconds before allowing the adhesive to cure.

The spring constant of the cantilevers was determined by measuring the resonant frequency of the cantilever before and after attachment of the calcite crystal [22].

Scanning electron microscopy (SEM) images of the tips were taken after calcite crystal attachments are shown in figure 1. The grown method produces a crystal more angled position than the attached method.

2.4 Atomic Force Microscopy Measurements

All AFM measurements were taken using a Dimension D3000 instrument (Veeco Instruments, CA). Force curves were obtained in synthetic hard water at 4 Hz frequency, with a scan size of 200 – 500 nm. 10 randomly selected positions were selected for each surface and 10 force curves taken at each position. Force curve analysis was performed using a specifically written MATLAB program.

2.5 Scaling Measurements

Scaling rate was determined in a rapid scaling test rig which consisted of a 1 L tank, a submerged heating element, covered by a removable sleeve and a temperature controller. Scaling rate was measured by conducting 10 heating and cooling cycles which consisted of heating the test solution to 70°C for 45 minutes and then allowing it to cool for 15 minutes. After 10 complete cycles the sleeve was removed and acid soaked to remove all the deposited scale and analysed through ICP-AES measurements

3. RESULTS

3.1 AFM Force Measurements

The force measurements taken with the modified probes are shown in figure 2. Generally there is good agreement between data obtained using the two probes. The gold and steel samples have a higher adhesive compared to the other materials. Interestingly there is more variation between these samples with the calcite grown as compared to the calcite attached probe. This is probably due to the orientation

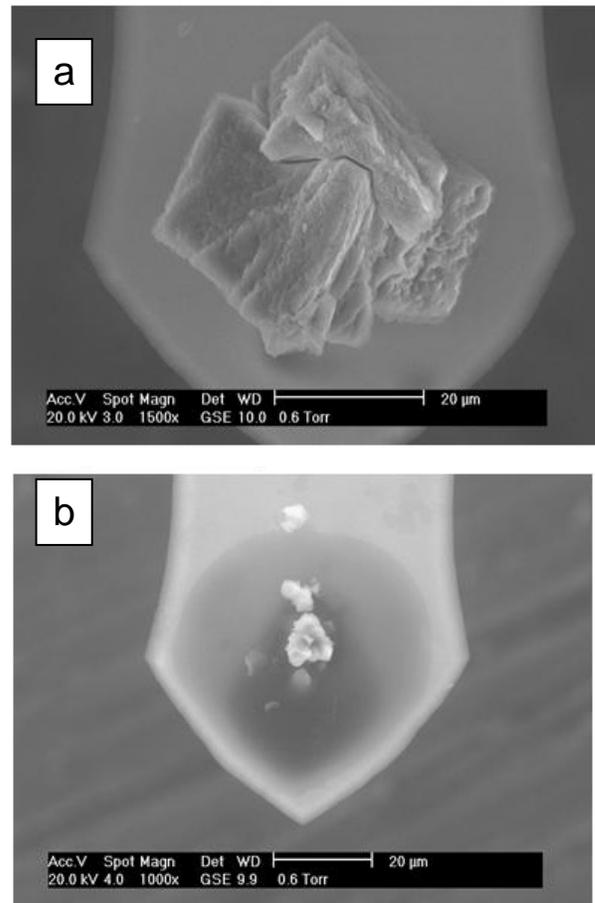


Fig 1: SEM images showing the modified AFM probes using calcite crystals (a) grown and (b) attached to the probe.

of the crystal on the grown tip which allows greater probing of the surface. Of the remaining surfaces, Dymon, DLC, Aluminium and PTFE, all have similar average adhesion force. By comparing the distribution of force (figure 3) then

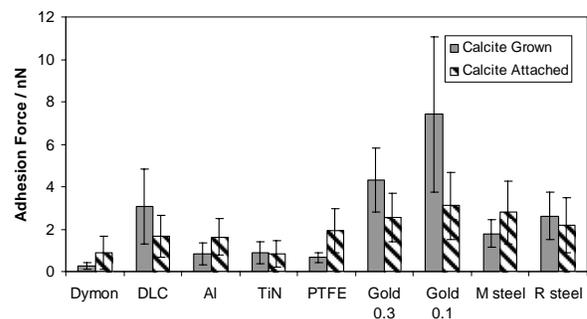


Fig 2: : A bar graph showing the average force for the adhesion between a calcite crystal and different materials, as measured using the atomic force microscope.

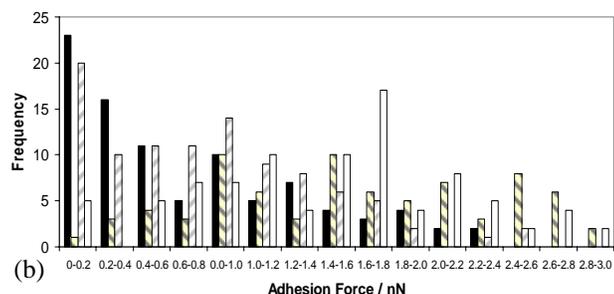
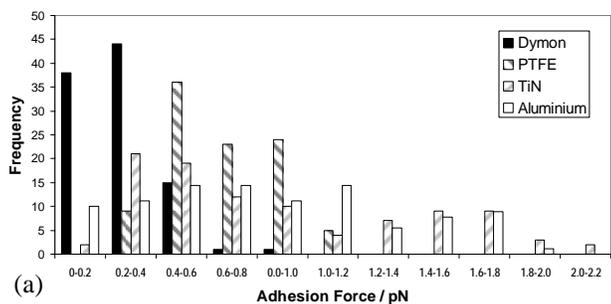


Fig 3: The distribution adhesion forces measured on several surface using (a) calcite grown and (b) calcite attached tips.

differences between the materials is apparent and for both types the pattern is the same. Dymon has the lowest followed by TiN, PTFE and aluminium measured using the atomic force microscope. The data was recorded in synthetic hard water and the measurements are an average of 100 force measurements.

3.2 Contact Angle Measurements

From the contact angle measurements the surface energy parameter of the surfaces could be determined and a theoretical work of adhesion with calcite can be calculated (Table I). Again Dymon and DLC surfaces have the lowest adhesive strengths although, surprisingly, aluminium and PTFE have the highest strengths.

3.3 Scaling Measurements

The measured scaling rates for all of the materials are shown in table I. The lowest scaling rates seen are for the diamond like carbon surfaces. The majority of the other materials have scaling rates in the 7 to 10 $\text{gm}^{-2}\text{h}^{-1}$ range, except for two surfaces gold 0.1 mm and R-steel which have rates of 12.78 $\text{gm}^{-2}\text{h}^{-1}$ and 14.10 $\text{gm}^{-2}\text{h}^{-1}$ respectively.

Substrate	Calculated work of adhesion to Calcite ($\text{mJ}\cdot\text{m}^{-2}$)	Scaling Rate ($\text{gm}^{-2}\text{h}^{-1}$)
Dymon	-7.2773	3.28
DLC	-1.898	3.42
Alum	11.3014	9.78
TiN	8.1456	8.26
PTFE	17.998	9.04
Gold 0.1	9.0852	12.78
Gold 0.3	6.5271	6.73
MS Steel	5.1344	8.33
RS steel	5.5099	14.20

Table I: Showing the calculate work of adhesion and scaling rate for each surface.

4. DISCUSSION

Comparisons of AFM force measurements with both contact angle and scaling rates are shown in figures 4 and 5 respectively. In both cases there is a board correlation between the parameters, admittedly with a large amount of scatter. This is significantly reduced by attaching the crystal onto the probe rather than growing it. The stronger bonding between crystal and probe in the formers case prevents movement of the crystal reducing the scatter of the results.

Theoretical adhesion forces assume adhesion in ultra pure water whereas the actual adhesion force, as well as for scaling mechanisms, occurs in hard water. Also contact angle measurements are very sensitive to impurities and changes in experimental conditions. These factors both could contribute to the deviation between adhesion force and work.

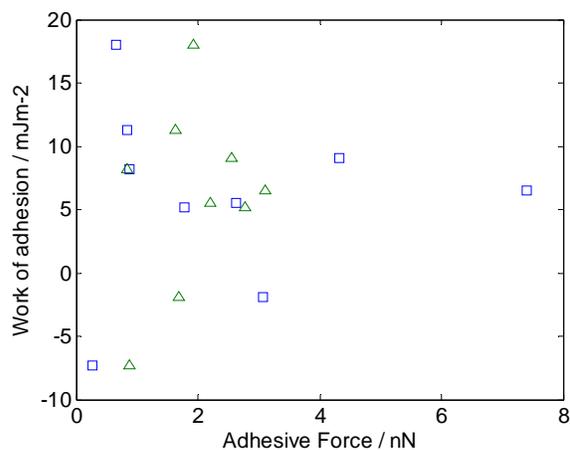


Figure 4: Graph showing the relationship between AFM adhesion force and the theoretical work of adhesion as calculated by contact angle measurements

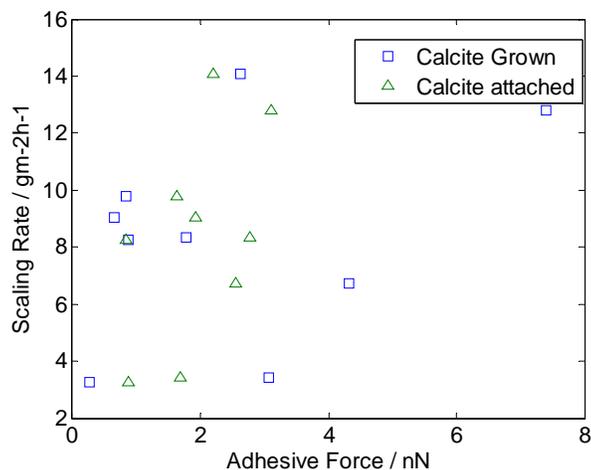


Figure 5: Graph showing the relationship between AFM adhesion forces and scaling rates

Scaling is a two stage process and the adhesion of calcite crystals, whilst an important it is not the only factor. In spite of this there is a relationship between the average adhesion force and scaling rate, but a closer one the distribution of adhesion forces. Figure 3 shows that for both types of probe the distribution follows the same pattern which mirrors the scaling rate. A surface may have a low average adhesion force but a higher than expected scaling rate if enough the calcite crystals adhere at a higher force. Similarly the opposite is true. So that the distribution of adhesion forces is as important as the average force when considering processes where adhesion plays an important role.

It has been demonstrated that nanoscale measurements can be related to macroscale phenomena. For scale formation it has been shown that there exists a relationship between crystal formation and layer formation. Hence materials scaling properties can be determined directly and quickly without the need for any costly trails.

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