Matching the nano- to the meso-scale: measuring deposit-surface interactions with atomic force microscopy and micromanipulation

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Abstract

Many researchers have studied the effects of changing the surface on fouling and cleaning. In biofouling the 'Baier curve' is a well-known result which relates adhesion to surface energy, and papers on the effect of changing surface energy to food fouling can be found more than 40 years ago. Recently the use of modified surfaces, at least at a research level, has been widespread. Here two different ways of studying surface-deposit interactions have been compared. Atomic force microscopy (AFM) is a method for probing interactions at a molecular level, and can measure (for example) the interaction between substrate and surfaces at a nm-scale. At a µm-mm level, we have developed a micromanipulation tool that can measure the force required to remove the deposit; the measure incorporates both surface and bulk deformation effects. The two methods have been compared by studying a range of model soils: toothpaste, as an example of a soil that can be removed by fluid flow alone, and confectionery soils. Removal has been studied from glass, stainless steel and fluorinated surfaces as examples of the sort of surfaces that can be found in practice. AFM measurements were made by using functionalized tips in force mode. The two types of probe give similar results, although the rheology of the soil affects the measurement from the micromanipulation probe under some circumstances. The data suggests that either method could be used to test candidate surfaces.

INTRODUCTION

The cleaning of process plant is a difficult multiscale problem; metre-scale plant becomes clean as a result of fluid and chemical action on surfaces of individual plant items, acting at the meso- and nano scale. A sketch of the different length scales involved in cleaning process plant is given as Figure 1. To remove deposit from surfaces is difficult both to understand scientifically and to do industrially (Wilson, 2005; Fryer *et al.*, 2006)

Fast moving consumer goods (FMCG) industries (food and consumer products) generally operate 'cleaning-in-place' (CIP) processes. Here, an automated system provides a set of programs to rinse and recirculate cleaning solutions through the equipment. Cleaning regimes have a number of environmental impacts, as use of chemicals, water, steam and energy causes an increase in the carbon footprint of the plant. Regular cleaning in-place can be very expensive in terms of downtime and materials (Tamine, 2008). To optimise cleaning time, it is essential to understand both the material behaviour during cleaning, and the removal mechanism.

A wide variety of fouling deposits are formed which require different cleaning fluids for their removal. Figure 2 shows a range of cleaning problems from the food and personal product industries, classified on axes depicting the type of deposit and the cost of cleaning chemical. Clusters of similar problems are found (Fryer and Asteriadou, 2009). The systems that are most difficult to clean are shown in the shaded area.

The severity of the fouling deposit differs depending on material properties:

- *low viscosity fluids*: here the fluid forming the 'deposit' is water or has properties close to water. This is found in the emptying of pipes and tanks containing milk or beer between process runs,
- *high viscosity fluids*: here the deposit is a highly viscous (perhaps viscoelastic) fluid, such as layers of toothpaste or shampoo left on the walls of process equipment, or starch from food sauces. The viscosity of these fluids may be several thousand times that of water,
- *cohesive solids*: here the fouling deposit behaves as a solid. Different deposits have very different material properties, ranging from the soft protein gel films formed from milk or other food fluids to the hard soils generated by precipitated minerals.

The properties of the deposit control the type of cleaning fluid needed:

- *cold water:* some soils are sufficiently weakly bound to the surface that they can be removed by rinsing with cold water alone.
- *hot water*: in personal products processing it is common to clean by circulation of hot water; removal is thus by fluid flow alone (Sahu *et al.*, 2007)
- *hot cleaning fluid*: many deposits are impossible to remove by water alone. Cleaning chemicals are thus used to speed the cleaning process and complex interactions between cleaning time, chemistry and flowrate are found (for example, Gillham *et al.*, 1999, 2000; Christian *et al.*, 2006).

The axes in Figure 1 are not in any sense numeric; the environmental cost of hot cleaning chemical is many times that of cold water. The aim of the process or product designer is to move away from the right hand side and top of the diagram. As part of a large industry-academia project ('ZEAL') we have studied a range of deposits from different industries, including brewery (Goode *et al.*, 2010), toothpaste (Cole *et al.*, 2010) and confectionery (Othman *et al.*,2010) soils.

Surface modification has often been proposed as a solution to the fouling problem (such as by Zhao *et al.*, 2005) and the differential adhesion of biofilms ('the Baier curve') to surfaces of different energy is well known (Baier, 1980). This curve shows that adhesion of bacteria to surfaces is minimised at some surface energy. Britten *et al.* (1988) studied the effect of surface coatings on dairy fouling, and found that interfacial energy of the surface appeared to be the main factor affecting the adhesive strength. Two more factors, discussed by Yoon and Lund (1994), are believed to affect fouling: (i) surface roughness, where the higher roughness the greater the contact area resulting in higher fouling rate and (ii) surface imperfections which provide more sites for crystal nucleation. For example Excalibur, a type of PTFE coating with a rough surface has been found to increase the fouling ability of a surface by 32% (Beuf *et al.*, 2003). Rosmaninho *et al.* (2007,2008) studied the adhesion of milk components under different flow conditions onto various surfaces and found that adhesion depended strongly on both surface and the deposit.

At present, the design of antifouling surfaces is empirical and has to be done on lab or pilot scales. The aim of this work is to identify whether it is possible to use surface analysis methods to quantify surface cleanability. A number of methods have been used to investigate the interactions between fouling materials and surfaces, in different industry sectors. Previous work on different fouling deposits and surfaces have used atomic force microscopy (AFM) to study surfaces, such as Parbhu *et al.* ,(2006) Santos *et al.* (2004), Verran and Whitehead (2006) and Whitehead *et al.* (2006). AFM is able both to measure surface topography and energetics over a nanometre to micron scale (such as in marine biofilms by Phang *et al.*, 2006, 2010) However there is very little work done in which AFM has been used to study food fouling problems.

A micromanipulation technique has been developed at Birmingham to quantify the forces involved in deposit removal at the micron-mm scale (Liu *et al.*, 2002, 2006ab, 2007). In this method, deposit is removed from the surface using a T-shaped probe connected to a force transducer which records the force needed as a function of time. Data can be expressed as the work required to remove deposit per unit area, i.e. in units of J/m^2. The same type of measurement can be made using dynamic gauging (Saikwan *et al.* 2006) where deposit is sucked from the surface by fluid action. The two give similar results (Hooper *et al.*, 2006). Saikhwan *et al.* (2006) and Liu *et al.* (2006a) studied removal using dynamic gauging and micromanipulation probes and found analogies to the Baier curve, in that adhesive failure occurred preferentially over a range of surface energies (22-28 mN/m) where surface binding was least strong.

The long-term goal of cleaning research is to generate systems that are inherently easier to clean – or which do not foul at all. This will require innovation both in the design of surfaces and of process plant. Obviously the measurement of the interaction between surfaces and deposits is important. Both AFM and micromanipulation methods can measure interfacial forces, but the relationship between them is unclear. The two measurement methods are both capable of giving numerical results for the strength of the forces involved in adhesion. It is not clear, however, whether the nano- and meso- scale can be compared, and whether the approach might be used to quantify cleanability.

In this paper, therefore, both AFM and micromanipulation have been used to measure the force required to remove four deposits from three surfaces of interest. As representative of actual FMCG deposits, toothpaste and confectionery deposits have been studied, and their interactions with stainless steel, glass and PTFE surfaces measured.

MATERIALS AND METHODS

Deposits and surfaces

The chosen deposits are from Types 1 and 3 in Figure 1: those removed by water alone (toothpaste) and those that require chemical removal (SCM, Turkish delight and caramel). Three surfaces were tested; glass, stainless steel and PTFE, which differ both in surface roughness (5.36 nm, 230 nm and 75.6 nm respectively) and surface energy (with water: 0.007 mJ/m^2, 0.075 mJ/m^2, 0.053 mJ/m^2; with sorbitol, the main toothpaste ingredient: 0.07 mJ/m^2, 0.07 mJ/m^2, 0.035 mJ/m^2), data from Akhtar (2010) .

The composition of the deposits was:

(a) Toothpaste contains: sorbitol, silica, saccharin, titanium dioxide, sodium lauryl sulphate, zinc citrate and water, (GSK, UK). Toothpaste is a suspension of different (titanium dioxide, zinc citrate, sorbitol and silica) particles that are approximately 0.5 µm in diameter.

(b) Confectionery deposits (all from Cadbury UK) were used, these were (i) caramel (glucose, sugar, whey powder, palm oil and water), (ii) turkish delight (agar, glucose, starch, sugar and water) and (iii) sweetened condensed milk (SCM) (sugar, butterfat, whey protein and water).

Stainless steel is widely used in the food processing industry, and PTFE is used here as representative of a 'non-stick' surface. Glass is widely used in the food industry as a hygienic surface to prepare and serve food.

AFM

Full experimental details are given in Akhtar (2010). Tipless Si cantilevers of nominal length 225 µm, nominal force constant 48 N/m and nominal resonance frequency of 190 kHz (Windsor Scientific, UK) were employed throughout this study. As it was easier to functionalise the tips with the surface materials than with the deposits, the experiments were conducted using the following materials as AFM colloid probes;

- Stainless steel 316L particles of 30 µm diameter (Reade, USA)
- Glass particles of 30 µm diameter (Polysciences, UK)
- Glass particles of 30µm diameter (Polysciences, UK) coated with a 200 nm thick film of vapour-deposited trichloro(3,3,3-trifluoropropyl)silane (hereafter referred to using the acronym TCTFPS, Aldrich, UK)

For each colloid probe, using the motorised stage on the AFM, each tipless cantilever was lowered into epoxy resin (Halfords, UK) to yield a small droplet on the underside of the cantilever upon retraction. The cantilever was then placed into contact with the desired microparticle and the adhesive allowed to cure. HPLC (High Performance Liquid Chromatography) grade water (Sigma-Aldrich, UK) was used for cleaning the modified tips.

The AFM was housed on a vibration isolation table to minimise the effect of ambient noise on imaging and measurement quality. Soil samples were deposited onto glass slides (Agar Scientific, UK) using a small syringe needle (Fisher Scientific, UK) prior to AFM analysis. All sample handling was carried out using Dumostar tweezers (Agar Scientific, UK) to minimise the risk of sample contamination.

All force measurements were performed in contact mode using a NanoWizard II AFM (JPK, Berlin). Force measurements were performed using the modified colloid probe cantilevers. Acquired real-time data was exported using JPK image processing software to provide cantilever deflections, and the peak pull-off force was calculated using Hooke's law by multiplying the peak deflection by the nominal cantilever spring constant. Peak pull-off forces were subsequently normalised against the radius of the probe tip, which was measured using the video camera system attached to the AFM.

Micromanipulation

The following model surfaces were used;

- Stainless steel 316L discs of 14 mm diameter and 1-2 mm thickness
- Stainless steel 316L discs of 14 mm diameter and 1-2 mm thickness, coated with 1 mm of TCTFPS
- Glass discs of 15 mm diameter and 1-2 mm thickness.

All discs were made at the University of Birmingham. A mass of 0.2 g of food deposits was spread uniformly over the whole surface of the discs. The initial thickness of the food deposit layer was approximately 0.7 mm. The SCM deposit layers were baked in a pre-heated laboratory fan oven at 80ºC for 1 hour, the other deposits were unbaked. The T-shaped probe was used to remove the food deposits at a constant speed of 1.1 mm/s. Gap widths (the height above the surface that the micromanipulation probe passes) of 20 µm, 100 µm, 200 µm, 300 µm and 400 µm were used.

The force required to remove the deposit was measured by drawing the micromanipulation arm across the surface of the deposit. From the force *F*, which changes with time, the total work, W (J) done by the applied force, *F(t),* to remove the deposit may be calculated as:

$$W = \frac{d}{(t_C - t_A)} \int_{t_A}^{t_C} F dt \tag{1}$$

where d is the diameter of the circular disc, and t_A and t_C the first and last times at which the probe touched the fouled surface. The apparent adhesive strength of a fouling sample, σ (J/m^2), defined as the work required to remove the sample per unit area of the surface to which it is attached, is then given by:

$$\sigma = \frac{W}{\alpha A} \tag{2}$$

where A (m^2) is the disc surface area, and α is the fraction of that area covered by the sample that can be measured by image analysis. In this case α is equal to 100%. The term ‘pulling energy’ is here used as not all of the deposit is removed in all cases, save for the lowest cut height above the surface.

RESULTS AND DISCUSSION

Atomic force microscopy

Caramel adhesion. Typical sets of results are shown in Figure 3, which displays data for the interaction between stainless steel and caramel taken in groups of five at different surface locations; this shows variation at the local scale (<10 mm) and between different points at 1-2 mm separations. The data shows that at the local scale of 10 µm, variation is relatively small (< ±0.05 N/m) while at a wider scale, variation is more substantial, with mean pull-off forces varying from 0.05 to 0.35 N/m. Data is plotted in terms of force over tip radius (F/R), which normalizes results from tips with different radii. This has the same units as the apparent adhesive strength defined above, although the two measurements are of different parameters. Errors are given as 2 standard deviations from the mean.

The pull-off forces between the surfaces and the food deposits are dependent upon the surface chemistry of both interacting bodies. The result depends both on the area of contact between the sphere and deposit, and the specific location on the deposit where the sphere makes contact. In general, the local variation was less than that over the wider area.

Figure 3(a) shows the pull off forces between glass, stainless steel and TCTFPS-coated microparticles attached to AFM tips immersed in caramel, for five different contact points. There is a clear difference between the forces measured for the three surfaces:

- a mean adhesive force of 0.4 (±0.02) N/m between glass and caramel, whereas
- stainless steel exhibited lower adhesive forces of 0.18 (±0.02) N/m, with
- the fluorinated, hydrophobic TCTFPS-coating exhibiting the lowest force of 0.04 (±0.02) N/m.

There is significant variation between the force measured at different points on the surface.

Adhesion of other species. Figure 4 (b)-(d) shows the adhesion behaviour of the combination of each microparticle and the other three deposits. The relative strengths of the interactions between each type of deposit and surface can be seen. For SCM, glass exhibits the largest adhesion, with stainless steel the next largest and very small adhesion forces for the TCTFPS coating. Interestingly, for Turkish delight the greatest adhesive force was measured against TCTFPS, although the maximum force is only 0.035 N/m. For toothpaste, glass again gives the largest adhesive force, again with much smaller adhesive forces.

Figure 5 summarises the adhesion data, which vary over two orders of magnitude, with F/R values varying between 0.3 and 0.001 N/m Greatest values are found with caramel and SCM, with smaller values for Turkish delight and toothpaste. Overall:

- the forces between the deposits and the glass microparticle show the largest adhesive behaviour with caramel, SCM, and toothpaste;
- the greatest adhesion between the TCTFPS-coated microparticle and the surface is seen for Turkish delight, although for both Turkish delight and toothpaste the forces are much lower than for the other two systems.

Micromanipulation

Figure 6 shows examples of the data obtained using the micromanipulation probe. For caramel, in Figure 6(a) the pulling energy (measured force per unit area from where deposit is removed) increases with increasing height above the surface and the slopes of the lines of pulling energy versus thickness are similar. At the lowest cut height (20 mm) deposit is fully removed from the surface, whilst at higher cut height some deposit is left on the surface. The value at the smallest cut height will have the greatest relevance in terms of surface adhesion force.. Stainless steel shows the highest pulling energy with slightly higher energies than glass, whilst TCTFPS shows the lowest interaction, of just over 4 J/m^2 at 20 mm. For the AFM data, shown in Figure 4, TCTFPS again gives lower adhesion forces. That the force required to remove the material increases with cut height implies that the force to remove the deposit from the surface is smaller than that required to cut the deposit in half, i.e. suggesting that the material is more likely to fail through fracture between surface and deposit. Toothpaste and SCM show similar trends as caramel where pulling energy decreases with increasing height (data not shown)

Figure 6(b) shows corresponding data for Turkish delight, showing (i) that the pulling energy required to remove the deposit decreases with increasing cut height, and (ii) that the largest energies are found for the TCTFPS surface, although the maximum of just under 3,5 J/m^2 at 20 mm is less than that of the caramel. That the pulling energy decreases with cut height suggests that it is easier to cut thin layers of deposit than thick ones, i.e. that removal would probably be from the top of the deposit rather than by adhesive failure.

Figure 7 shows the data sets for the micromanipulation experiments, plotting the results to remove the deposit for a cut height of 20 microns, i.e. where the cut is closest to the surface, and where the force measured will be most related to the surface-deposit interactions. In three out of the four cases, stainless steel has the highest measured force, whilst for the Turkish delight, the largest force between deposit and surface is found for the TCTFPS.

Comparison.

Both methods can be successfully used to get an idea of interfacial forces. Figure 7 can be usefully compared with Figure 5. The clear difference is that a log scale is needed to visualise the variation in the force values seen for the toothpaste and TCTFPS data, whilst the results of Figure 7 do not show the same magnitude of variation with values between 2 and 12 J/m^2. The micromanipulation measurement records the force required to remove the deposit from the surface, and thus measures both the surface-deposit interactions and some measure of the rheology of the deposits and how they deform. AFM is a more precise measurement, which measures only surface-deposit interactions. The difference in the ranges of the two measures suggests that the magnitude of surface interactions varies by a larger amount than is shown by the micromanipulation measurements. Figure 8 displays the results for the two methods directly, plotting pulling energies against F/R, again showing that the data follow the same trends.

The data for the two measurement systems compares well:

- for Turkish delight, both AFM and micromanipulation data record that the fluorinated surface shows the greatest adhesion; this agreement shows that both techniques can be used to assess adhesion forces between substrates and soils
- data for stainless steel and glass are more closely matched, but forces measured are greater than that for the fluorinated surfaces for caramel, SCM and toothpaste. The micromanipulation measures forces for stainless steel as being larger than for glass, whilst AFM records the opposite, perhaps the difference in micron-scale roughness of the two is responsible for this effect.

The experiments suggest that micromanipulation data can provide information related to the detail shown in the AFM. That the surprising result for the Turkish delight is measured by both systems suggests that they are measuring similar effects, albeit at different length scales.

AFM is a more sensitive measurement method than micromanipulation, and more parameters are required to set up experiments, such as the need for the right size particle and the right cantilever stiffness. Also it is not known until the experiment is performed how much vertical range is required in the AFM. In comparison micromanipulation is relatively simple to use and set up and most deposits are easily compatible, compared to the AFM. Many of the surfaces being developed are however first made at the nm scale – these results suggest that it would be possible to predict meso-scale behaviour from atomic scale measurement.

Fryer and Asteriadou (2009) have suggested a possible classification of deposits, which could be useful if it allows decisions to be made about selection of cleaning protocols. Deposits which fail adhesively – by failure at the interface between the deposit and the surface - may well need to be treated differently from those, which fail due to breakdown of cohesive interaction (Liu, *et al.* 2006ab).

CONCLUSIONS

This paper describes experiments in which two method of measuring the forces, which bind fouling deposits to surfaces have been compared. Atomic force microscopy works at the nano-scale, whilst micromanipulation measures the forces between layers of deposit some mm thick and the surface. A series of deposits (toothpaste, caramel, Turkish delight and sweetened condensed milk) have been studied which are relevant to problems in the personal care and confectionery industries.

AFM force measurements were performed using modified tipless Si cantilevers attached with a microparticle of different surfaces; the tip was engaged to the sample and force measurements taken. Micromanipulation experiments required 0.2 g of Turkish delight, caramel, SCM and toothpaste to be uniformly spread over the whole surfaces for removal.

The two methods give comparable results; however the range of forces measured by the AFM is much greater, reflecting that the micromanipulation measurement includes the force required to deform and displace the whole deposit.

AFM and micromanipulation are both beneficial tools for the measure of adhesion. AFM works at the nm-scale whilst micromanipulation measures at the µm-mm scale. It is clear that, as found by other workers, the surface energy affects the force required for removal. The advantage of the AFM is that this is an instrument, which is commonly used in the development and characterisation of new materials, which may initially only be available in very small quantities. Measurements using such small samples have been shown to be a good prediction of macroscale behaviour – this may help material designers identify potentially new antifouling surfaces without having to do experiments at higher scale.

ACKNOWLEDGEMENTS

This paper reports results from the ZEAL project TP//ZEE/6/1/21191, which involves; Alfa Laval, Cadbury Ltd., Ecolab Ltd., Newcastle University, Scottish & Newcastle Ltd., GEA Process Engineering Ltd., Unilever UK Central Resources Ltd., Imperial College of Science Technology and Medicine, GlaxoSmithKline, Bruker Optics Ltd. and the University of Birmingham. The project is co-funded by the Technology Strategy Board's Collaborative Research and Development programme, following open competition. For more information visit <http://www.innovateuk.org>.

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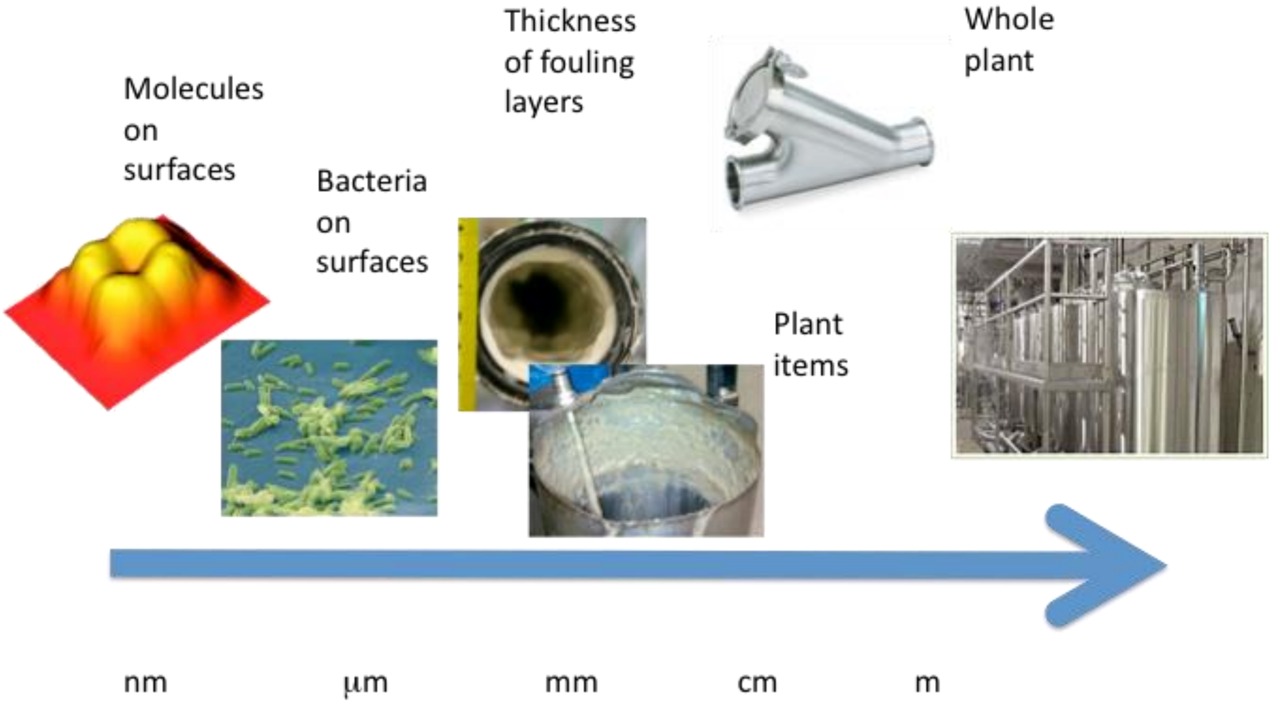


Figure 1. Illustration of the different length scales of fouling and cleaning, from nm molecular interactions to the m-scale of process plant.

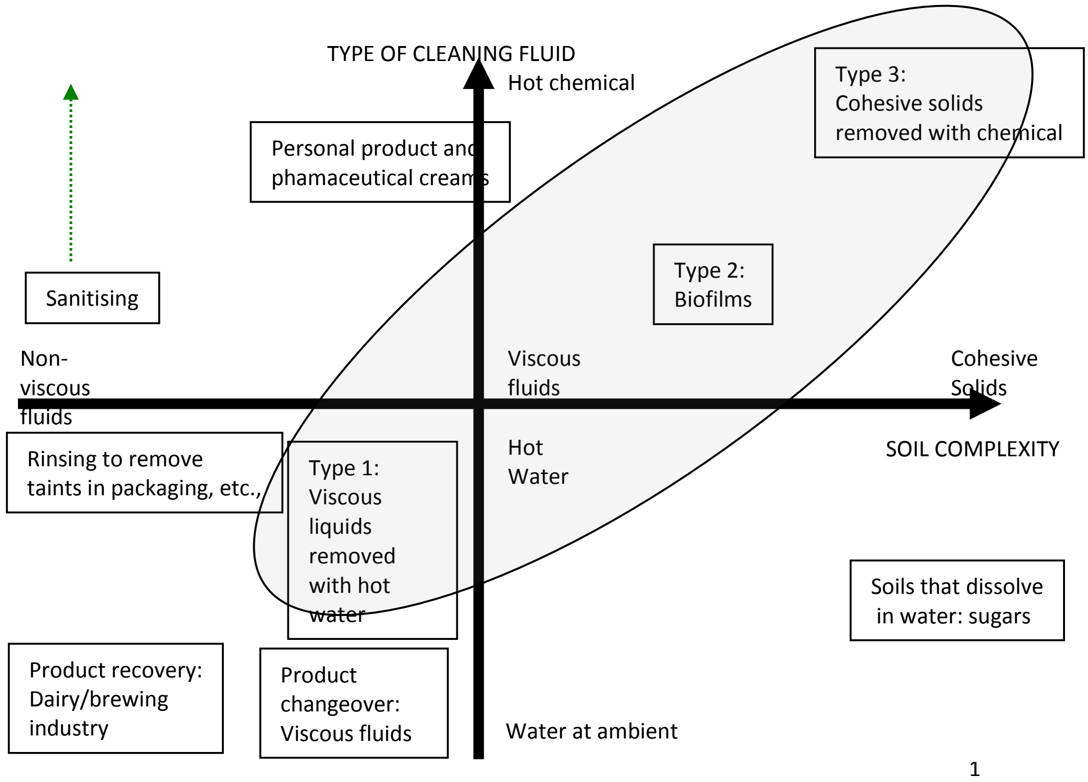


Figure 2. Cleaning map: shows a range of cleaning issues from the food and personal product industries, demonstrating that clusters of similar problems are found. The systems that are most difficult to clean are shown in the ringed area (from Fryer and Asteriadou, 2009).

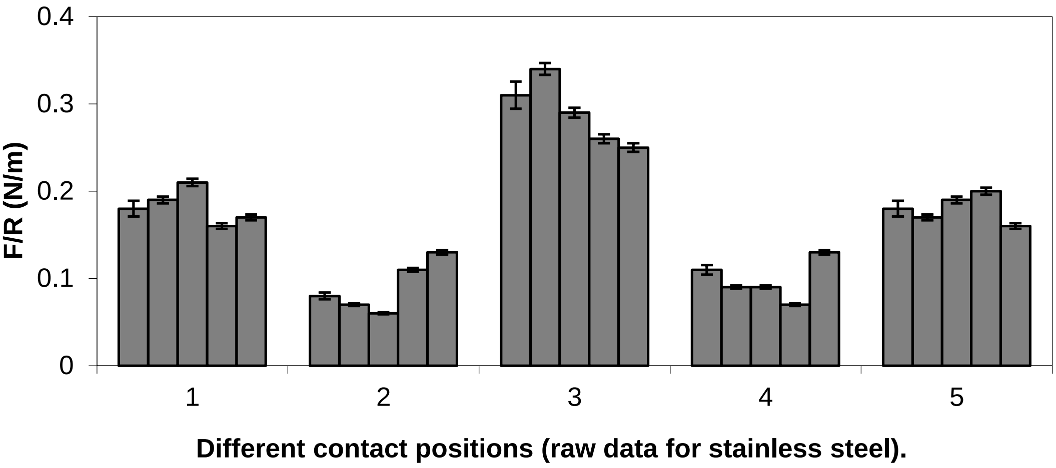
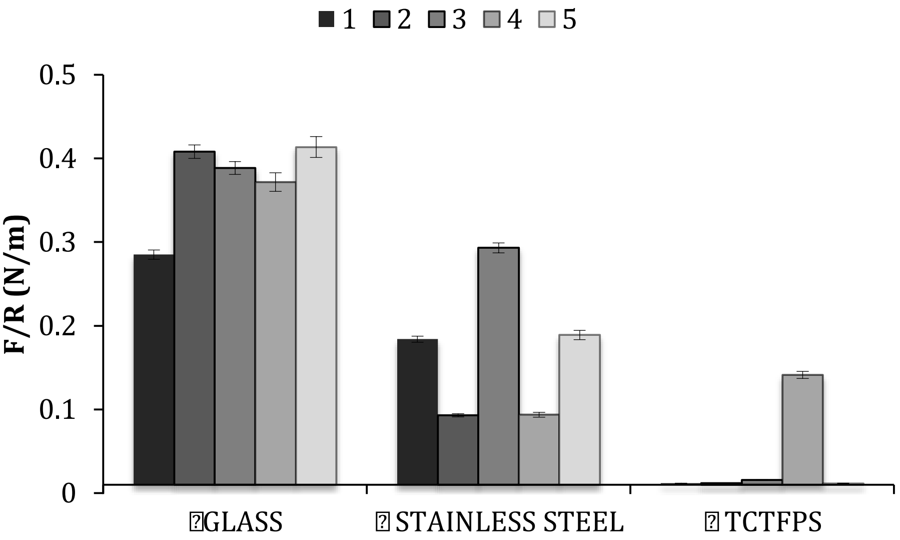


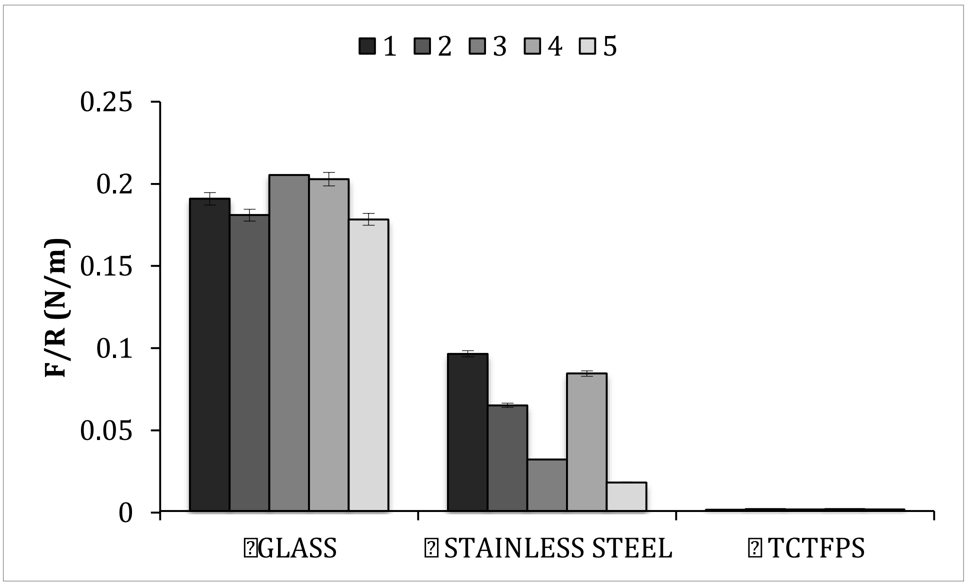
Figure 3. Interaction between stainless steel microparticles and caramel, measured using the AFM. Data shows local variation of 5 points at each of the 5 regions on the caramel deposit; error bar shows the equipment error per measurement.

caramel



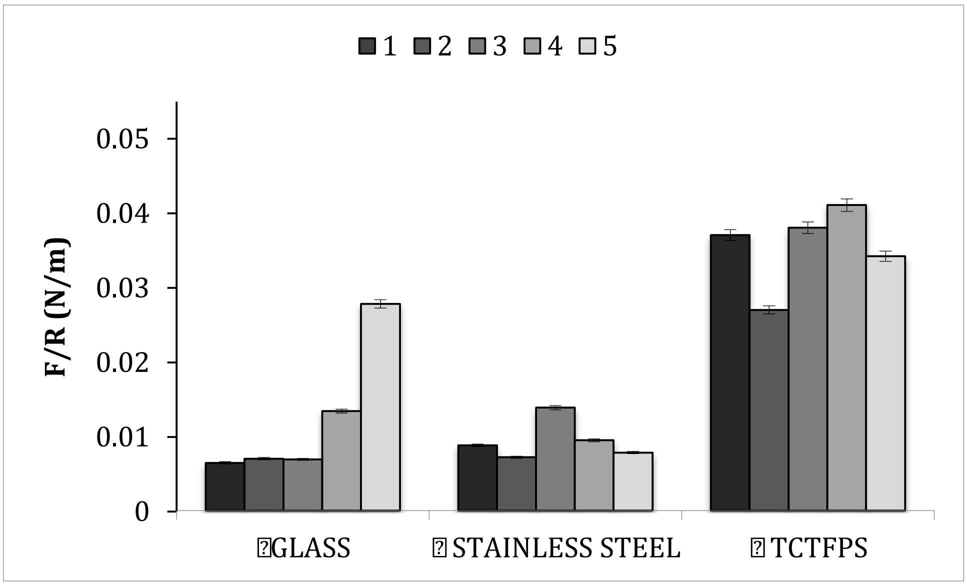
(a)

SCM



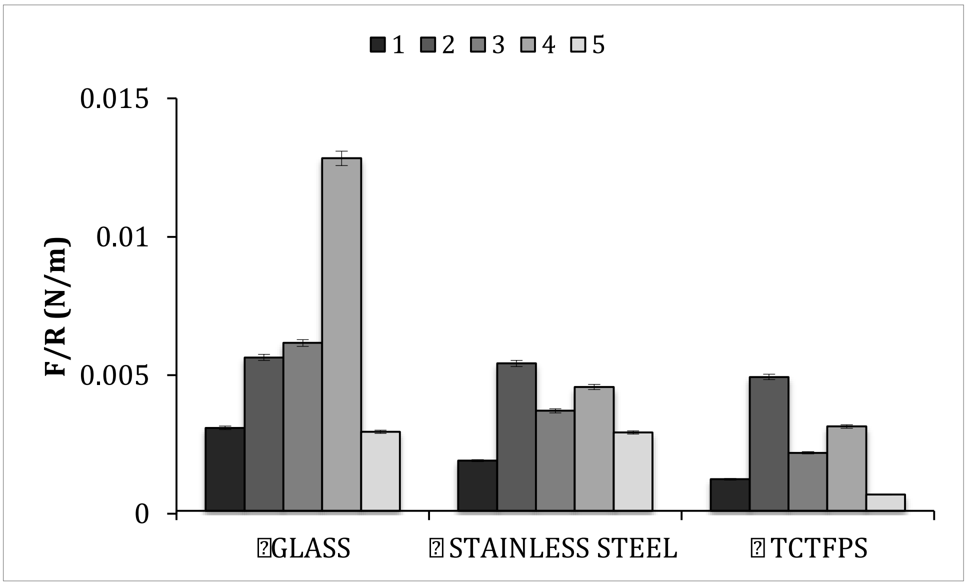
(b)

Turkish delight



(c)

toothpaste



(d)

Figure 4. AFM force measurements. Glass, stainless steel and TCTFPS microparticles were immersed in deposits and then retracted. Deposits were spread 50 - 60μm thick on a glass slide. Data shows results from five different contact positions (1-5) on the deposits. The approach speed for all experiments was 3μm/s, followed by a 5 second pause on deposit and 0.25μm/s retract. Deposits are (a) caramel, (b) SCM, (c) Turkish delight, (d) toothpaste;

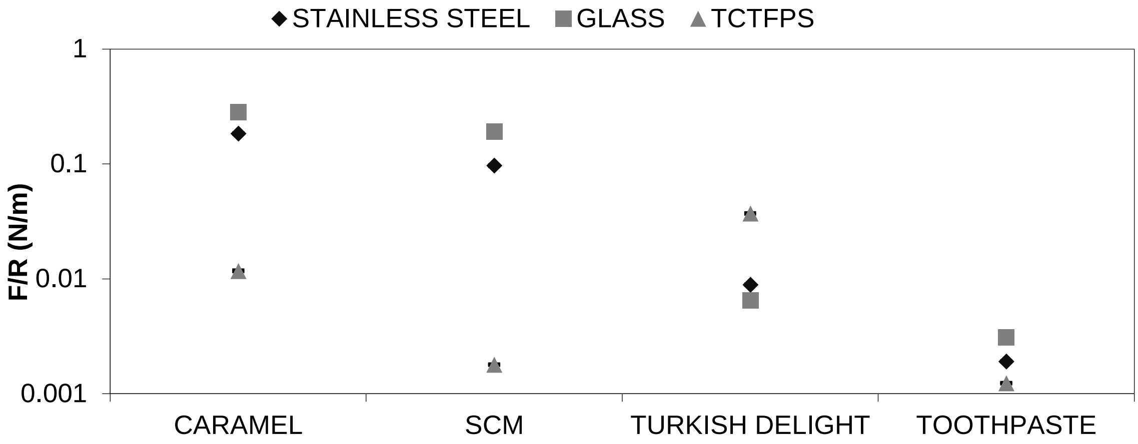
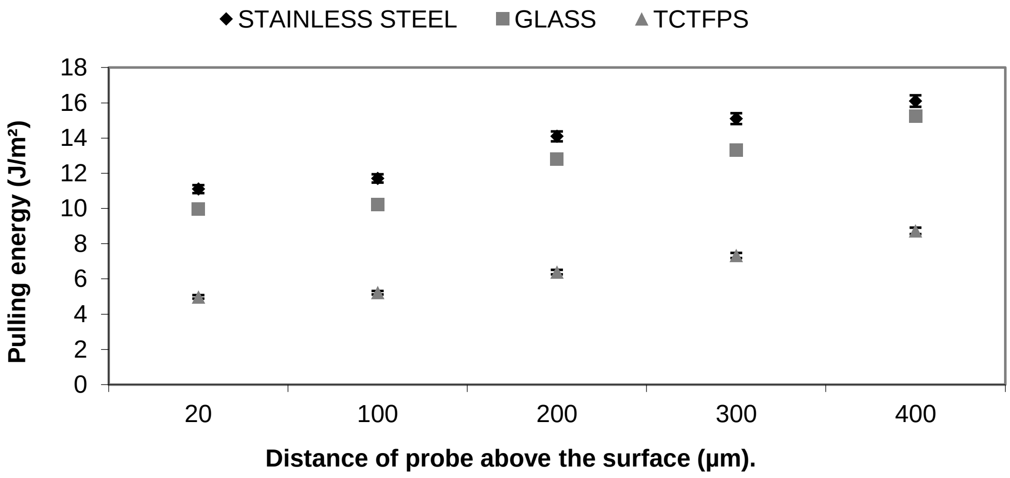


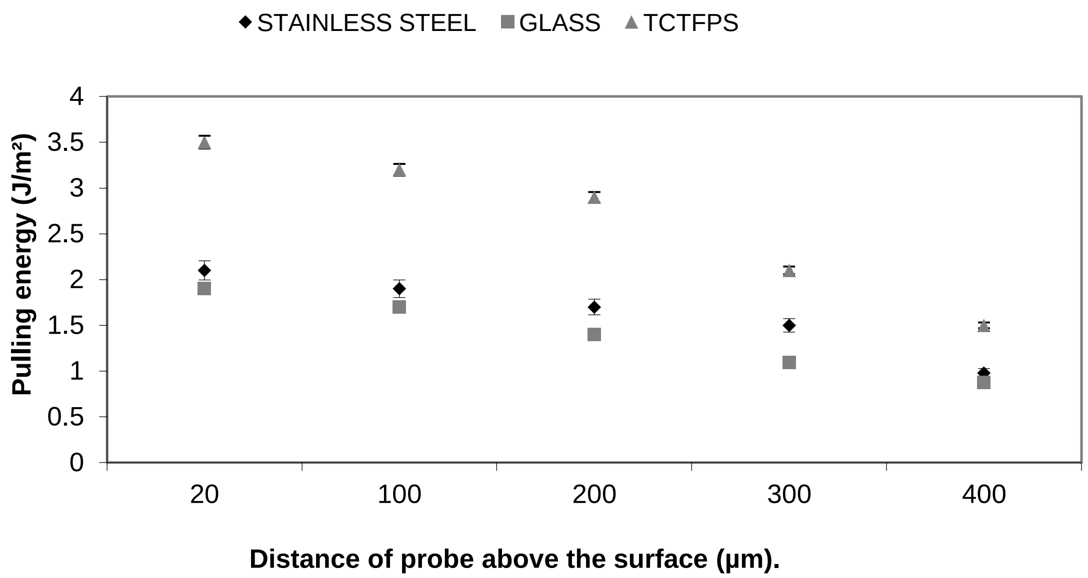
Figure 5. A summary of the forces measured by AFM for the different microparticles and all four deposits.

caramel



(a)

Turkish delight



(b)

Figure 6. Pulling energy for removal of (a) caramel deposit and (b) Turkish delight, using the micromanipulation probe. The gap between probe and substrate was kept at 20, 100, 200, 300 and 400μm, the surfaces used were stainless steel, glass and TCTFPS.

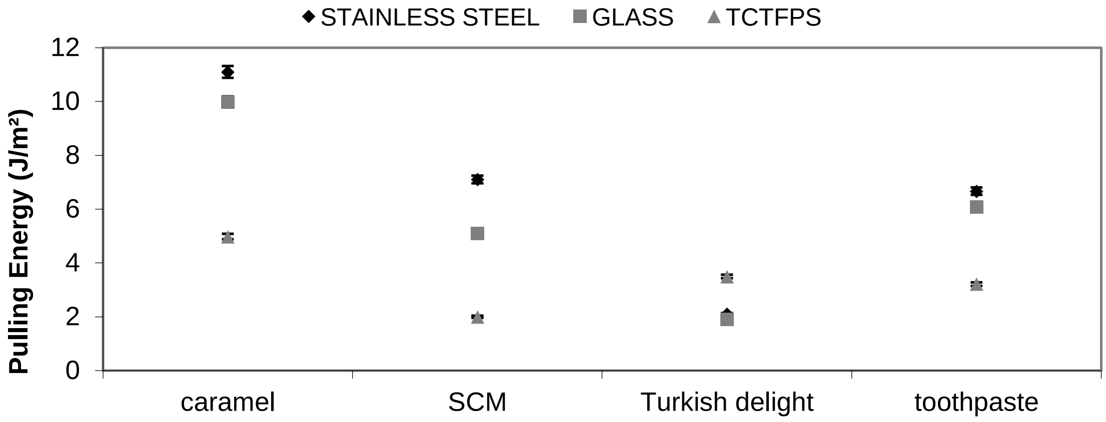


Figure 7. Summary of micromanipulation experiments at 20µm cut height of caramel, SCM, Turkish delight and toothpaste on glass, stainless steel and TCTFPS.

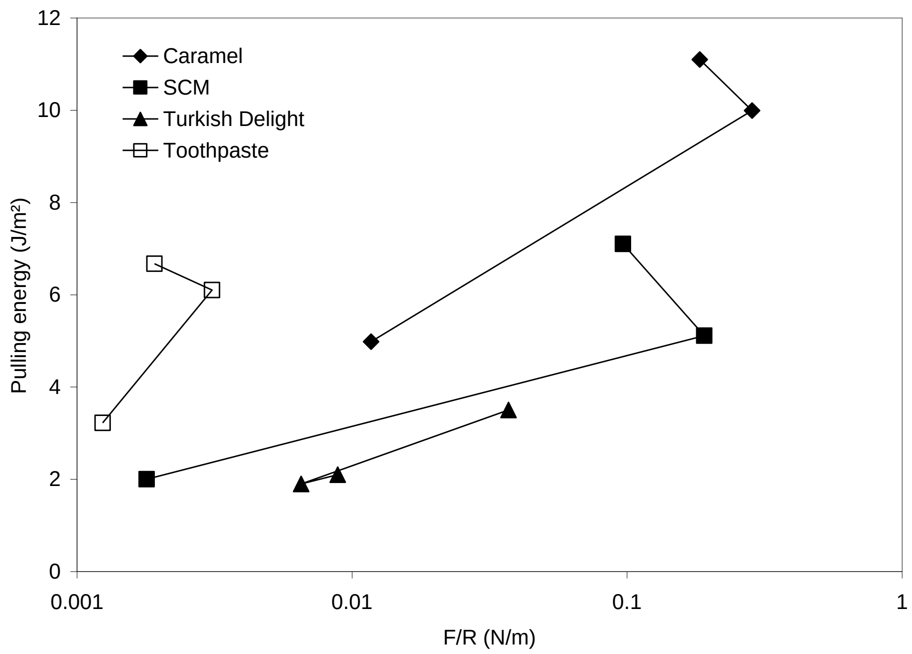


Figure 8. Comparison of data from micromanipulation and AFM, plotted for each deposit type.