

1 Quantifying the effect of solution formulation on the removal of soft solid food
2 deposits from stainless steel substrates

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33 *Abstract*

34 The role of detergent formulation on the cleaning of a complex carbohydrate-fat food
35 soil from stainless steel surfaces was studied using a modified version of the
36 millimanipulation device described by Ali *et al.* (2015b) which allowed the force
37 required to scrape the soil from the surface to be measured as the soil is immersed, in
38 situ and in real time. This allowed the influence of temperature, solution chemistry and
39 time on the mechanical forces (rheology) and removal behaviour of the soil to be
40 studied – in effect quantifying the relationships in Sinner’s cleaning circle. The soil
41 simulated a burnt-on baked-on deposit and featured regular cracking in the 300 µm
42 thick layer. The removal force decreased noticeably on hydration: the cleaning
43 mechanism was then determined by the agents present. At 20°C, below the temperature
44 at which the fat phase was mobile, removal was characterised by cohesive failure except
45 in the presence of the cationic surfactant CTAB, which promoted adhesive failure and
46 fast decay in removal force. At 50°C, when the fat was mobile, a transition between
47 cohesive and adhesive failure was observed at pH 7 which was inhibited at higher pH.
48 Adhesive failure and fast decay in removal force was observed at higher pH and 50°C
49 in the presence of the anionic and non-ionic surfactants, SDBS and TX-100,
50 respectively.

51 *Keywords* Millimanipulation, cleaning, adhesion, burnt soil, surfactant

52

53 **Introduction**

54 Fouling and cleaning is ubiquitous in the food sector, from the domestic kitchen to large
55 scale manufacturing plants. The first commercially available electrical dishwasher was

56 sold in the 1920s and improvements to their effectiveness have been achieved both by
57 optimising the water cycling system (e.g. Rosa *et al*, 2012) and developing
58 combinations of cleaning agents in the ‘detergent’ to clean more quickly and impart
59 dishes with ‘shine’ (Showell, 2005; Rosen and Kunjappu, 2012).

60 Significant advances have been made in the understanding of the cleaning mechanisms
61 of single-component food soils over the past 20 years. Soils studied include whey
62 protein gels (Saikhwan *et al*, 2010), heated egg white (Li *et al*, 2015), milk deposits
63 generated during thermal processing (both pasteurisation and higher temperature
64 operation, e.g. Morison and Thorpe, 2001), mixtures of commercially available cooking
65 oils (Jurado-Alameda *et al*, 2015), and starches (Otto *et al*, 2016). The cleaning
66 mechanism is dictated by the composition and structure of the soil (Fryer and
67 Asteriadou, 2009) and those listed all differed noticeably.

68 For example, the wheat starches studied by Din and Bird (1996) were cleaned via
69 enzymatic breakdown of the starch polymers into dextrans, oligosaccharides and sugars,
70 each of which are more soluble in water than the parent molecule (Pongsawasdo and
71 Murakami, 2010). Jurado-Alameda *et al*. (2015) found that surfactants such as linear
72 alkylybenzylsulphonate (LAS) had little impact on the rate and extent of cleaning of
73 dried potato starch residues on stainless steel fibres. In the absence of amylases, high
74 pH and long soaking times were required for cleaning regardless of surfactant
75 concentration. The use of heated solutions gave more benefit than other factors at room
76 temperature. Such information is often discussed in terms of Sinner’s cleaning circle
77 relating how time, temperature, chemistry and mechanical forces together determine
78 how well and how fast different soils can be removed from a surface.

79 Protein-containing soils generated by cooking often contain thermally denatured gels.
80 These swell and may be broken down following contact with alkali, and cleaning can
81 involve dissolution or erosion, both of which can be diffusion limited (Morison 2002).
82 The erosion of heated whey protein deposits can be enhanced by flow pulsing (Gillham
83 *et al*, 2000) or regular switching between cleaning solutions (Christian and Fryer 2006).

84 Oils have been found to be the most difficult of all common foodstuffs to clean (Detry
85 *et al*, 2007, 2009; Palmisano *et al*, 2011) owing to their inherent hydrophobicity and
86 tendency to wet many dishwares preferentially to water. Fatty soils pose a particular
87 challenge as most consumer detergents employ aqueous solutions. The active agent

88 must therefore be soluble (or encapsulated) in water, preferentially adsorb on to the soil
89 surface, remove the soil from the substrate, and stabilise removed residues in the
90 solution. Highly polymerised lipids such as those found in burnt oil soils have limited
91 solubility in organic solutions and no recorded solubility in water (Ali *et al*, 2015a).
92 High pH or long soaking times are often required, in combination with mechanical
93 shear, to remove such soils from the substrate (Dunstan and Fletcher, 2014). Surfactants
94 can promote detachment of mobile components at the soil-substrate interface (Ali *et al*,
95 2015a, 2015b). A combination of saponification, mechanical cleaning and surfactant
96 action will be required to clean burnt oil soils as the existing literature does not report
97 a single mechanism being entirely effective.

98 Other techniques promoting cleaning include modification of the substrate, either
99 temporarily, such as adjusting the electrostatic charge of a stainless steel surface
100 (Mauermann *et al.*, 2009) or permanently via coating (Ashokkumar and Adler-Nissen,
101 2011; Magens *et al.*, 2017). These approaches are suited for repeated processes where
102 the soil and substrate operations do not change: with multi-product plant (or facilities
103 such as a kitchen) one substrate may enhance cleaning of one soil and promote adhesion
104 of another (Ali, 2015).

105

106 *Baking and drying*

107 The properties of the soil to be cleaned are determined both by its composition and its
108 processing history, and particularly its thermal history (Fryer and Asteriadou, 2009).
109 Thermal transformation is widely used in food processing (baking, drying, frying, ...) and
110 exposure to high temperatures, often in humid environments, promotes
111 evaporation, shrinkage, and chemical reactions including free radical polymerisation,
112 condensation polymerisation and thermal decomposition. These structural changes
113 encourage closer packing which increases the cohesive forces in the soil (Stanga, 2010).
114 This paper considers baked mixtures of proteins, fats and starches (with small amounts
115 of minerals and fibres).

116 Drying (typically at 85-90 °C for 1 hour) has been shown to increase soil adhesion.
117 Marked increases in both the cohesive and adhesive strength of starch soils following
118 water loss were reported in ultrasound cleaning studies by Stanga (2010) and dynamic
119 mechanical analysis measurements by Jonhed *et al.* (2008). Surface energy studies by

120 Otto *et al.* (2016) demonstrated that whilst starch underwent structural changes during
121 heating, whey and soy proteins exhibited a significantly larger response to heating as
122 measured by UV-Vis photometry in a continuous flow cleaning system. Protein
123 denaturation caused by heating for an hour at temperatures above 55 °C caused internal
124 hydrophobic structures to become exposed, accompanied by a large shift in the Lifshitz-
125 van der Waals component of the soils surface energy measured for those soils. This
126 leads to strong wetting and adhesion on stainless steel surfaces. The additional exposure
127 of internal binding groups such as sulfhydryl allows disulphide bridges to form on
128 drying, forming denser, more cohesive soils on the substrate (Castner and Ratner,
129 2002).

130 In this work the soiling layers were baked at 204 °C for 7 minutes, so that virtually all
131 the water initially present is evaporated off and the above structural changes are
132 accompanied by reaction steps. These burnt complex soil layers pose particular
133 challenges for cleaning and the aim of this work is to generate insights into how
134 particular cleaning agents or mixtures thereof achieve soil weakening or removal of
135 multi-phase soils comprising of burnt starch-protein-fats solid networks surrounded by
136 more mobile fats.

137

138 *Soil Adhesion Forces*

139 Sinner's circle allows information about cleaning to be linked qualitatively, and there
140 is a need to quantify the effect of chemistry and temperature on removal. For soils which
141 do not dissolve, the response to mechanical forces, *i.e.* their rheology, needs to be
142 quantified, preferably *in situ* and in real time.

143 Cleaning ultimately involves disruption of soil-substrate bonds. Soils bind through a
144 combination of Lifshitz-van der Waals, ionic and electrostatic forces (Moeller and
145 Nirschl, 2017). In dry conditions Lifshitz-van der Waals tend to dominate (Kumar *et al.*,
146 2013) but when immersed in aqueous solution, electrostatic forces, influenced by
147 factors such as pH and electrolyte concentration, play a larger role (Israelachvili,
148 1998). Prochaska *et al.* (2007) reported that cationic starches had a stronger binding
149 potential to stainless steel than natural starch, and attributed this to differences in ionic
150 interactions with the steel surface which, when submerged in water, acquire a negative

151 charge. Determining the impact of cleaning agents on the balance of all the above
152 interactions provides insight into the cleaning mechanisms and thus development of
153 more effective dishwashing formulations through targeted selection of agents for
154 components which are difficult to remove (Basso *et al.*, 2017).

155 Measurement of the forces required to clean, *i.e.* detach elements of soil from a
156 substrate in a given environment is currently performed at three length scales of
157 investigation: the nano-, micro- and macro-scales.

158 Macroscale testing of cleaning performance is the most widespread approach as it
159 underpins empirical investigation and supports direct transfer of results to practice.
160 Cleaning-in-place (CIP) systems are widely used to ensure the hygiene of food
161 manufacturing plant, and scaled down systems have been used to investigate such
162 operations. Interpretation of the results in terms of cleaning mechanisms can require
163 detailed analysis which is not always straightforward. The bath-substrate-flow system
164 employed by Jurado-Alameda *et al.* (2015) allows the effect of solution formulation to
165 be studied but the flow regime in the cell is complex so identifying the dependency on
166 local flow velocity (and hydraulic forces) is difficult. Flow cells (*e.g.* Bishop, 1997;
167 Detry *et al.*, 2007; 2009) are often used to study the impact of shear forces in cleaning
168 as the fluid flow patterns are known or can be predicted numerically, so that the results
169 can be related to the process scale.

170 At the other end of the spectrum, nano-scale investigations typically involve measuring
171 the adhesive forces between well-defined elements of a test soil and a surface. Aktar *et al.*
172 (2010) used an AFM cantilever to measure the adhesion force¹ associated with
173 removal of caramel particles from stainless steel and recorded values in the range of
174 0.1-0.3 N m⁻¹. Bobe *et al.* (2007) reported similar values, of 0.21 – 1.3 N m⁻¹, for
175 removal of yeast particles from stainless steel surfaces. These forces depended on
176 particle size and the distance of the tip from the soil. Such techniques can provide
177 valuable insight into the chemical and electrostatic forces active in soil-substrate
178 binding, and in attachment of spores and bacteria (*e.g.* Lelièvre *et al.*, 2002).

¹ Adhesion forces are reported in N m⁻¹: this quantity is equivalent to surface energy, in J m⁻²

179 Food soils tend to be multicomponent and microstructured, subject to variations in
180 topology, morphology and electrostatic environments across the substrate at the length
181 scale of 10 – 100 μm . Additional information on interactions is required for such
182 systems and researchers have therefore tended to focus at the micro-scale. Moeller and
183 Nirschl (2017) deposited approximately 1000 particles of starch-based soil onto a
184 stainless steel surface and measured the centrifugal force required to remove them. This
185 allowed statistical treatment of the results from a test of reasonable duration. They
186 found that the repeatability of the method was highly dependent upon the soil type and
187 structure: the more complex the soil the lower the repeatability. In this paper tests are
188 performed in triplicate in order to create higher confidence in the repeatability of the
189 results. This number of tests does not support a rigorous statistical analysis.

190 Surface roughness has also been shown to lead to variability in testing at this length
191 scale. Hauser (2008) reported a decrease in adhesive strength between soil and substrate
192 with increasing roughness but also a decrease in cleaning efficiency in immersed
193 systems. Bobe *et al.* (2007) pointed out that measures of roughness such as R_q provide
194 no information about the ‘structure’ of the roughness elements, *e.g.* spherical vs
195 cylindrical vs conical, which play an important role in adhesion. Quantifying roughness
196 and relating it to adhesion forces continues to be an active topic of investigation,
197 promoted by the advent of nano-fabrication and tailoring of surfaces (LaMarche, 2017).

198 A number of micro-scale devices have been developed for studying the forces involved
199 in cleaning under chemical environments and differences between soil components.
200 These typically involve imposing a known shear force or shear stress on the layer and
201 measuring the resulting deformation, or imposing a deformation *etc.* Fluid dynamic
202 gauging (FDG) is an example of the former and has been used to monitor the strength
203 (Chew *et al.*, 2004) and swelling characteristics (Gordon *et al.*, 2010) of food soils when
204 contacted with a variety of cleaning solutions. Whereas denatured whey proteins were
205 reported to swell and erode in alkali, gelatin and egg proteins both swelled but both
206 require shear forces to effect removal (Gordon *et al.*, 2010; Perez-Mohedano *et al.*,
207 2016). Ali *et al.* (2015a) observed little swelling with burnt oil soils in aqueous cleaning
208 solutions and removal of these was characterised by a ‘cohesive blistering’ mechanism.
209 The size and quantity of blisters formed per sample depended upon the solution pH and
210 the shear forces generated by agitation of the solution.

211 The use of controlled deformation (effectively controlled strain) devices was pioneered
212 by workers at Birmingham (Liu *et al.*, 2002) who adapted a micromanipulation device
213 originally developed for studying individual yeast cells (Marmoushy *et al.*, 1998) to
214 study the removal of biofilms and soil layers. Liu *et al.* (2002) identified and quantified
215 different failure modes between soil types: baked tomato paste removal was dominated
216 by its cohesive strength, exhibited by its detachment in chunks even after soaking in an
217 external bath, while pure whey protein deposits exhibited predominately cohesive
218 failure.²

219 Micromanipulation tends to work at scale of tens of microns, and the heterogeneity of
220 food deposits prompted workers such as Ashokkumar and Adler-Nissen (2011) and Ali
221 *et al.* (2015b) to develop ‘millimanipulation’ devices which could be used to study
222 composite deposits, as well as hard layers which techniques such as FDG could not
223 deform. Those workers considered dry deposit layers. In this work, the device presented
224 by Magens *et al.* (2017) was adapted to allow immersion of the sample in cleaning
225 solutions for controlled lengths of time, at temperatures ranging from 20 °C to 50 °C,
226 mimicking the chemical environment in a domestic automatic dishwasher. The soil
227 studied is a complex mixture of starch, protein and fat, representative of some
228 encountered in practice. The measurements provide indications of the rheology and
229 cleaning behaviour of the soil, immersed in cleaning solution, *in situ* and in real time
230 and thereby provide direct quantification of the effects of the parameters in Sinner’s
231 cleaning circle.

232

233 **Materials and Methods**

234 *Soils and substrates*

235 A model burnt soil deposit, henceforth referred to a complex model soil (CMS), was
236 generated containing fats, carbohydrates and proteins as detailed in Table 1. This
237 formulation was provided by Procter and Gamble to mimic consumer products known
238 to pose difficulty in automatic dishwashers. The soil was applied as a slurry to stainless
239 steel substrates, dried and baked.

240 ² There is a difference in terminology between Liu *et al.* (2002) and this paper. Liu *et al.* described a
241 soil as failing cohesively when the adhesive strength of the soil to the substrate is lower than the
242 internal cohesive strength of the soil. Here, cohesive failure is used to describe the case when the
243 cohesive strength of the soil is lower than the adhesive strength of the soil to the substrate.

244 Slurry preparation involved boiling the pasta in deionised water for 7 minutes before
245 draining the liquid off and adding the solids to the fat emulsion (pre-heated to 50 °C),
246 milk, cheese powder and salt. The mixture was then blended for 1.5 minutes at
247 maximum speed on a household food processor (Cookworks, HA-3213) until it
248 appeared homogenous to the eye. An excess of the slurry was placed on the sample
249 plate and a wiping blade device (Supplementary Figure S1) similar to that reported by
250 Glover *et al.* (2016) was used to generate a smooth layer of initial thickness δ . The gap
251 between the blade and the substrate is set by a pair of micrometers with a precision of
252 $\pm 1 \mu\text{m}$: the dried layer was rougher than this owing to the inherent heterogeneity of the
253 slurry. δ was typically 300 μm and the layer mass approximately 1.8 g, giving an initial
254 coverage on 50×50 mm test plates of 0.72 kg m⁻².

255 The sample was then left to dry in air (20°C, 48 % humidity) for 24 hours before being
256 baked in air in a conventional oven at 204 °C for 7 minutes. Baked samples were left
257 standing in ambient air to cool to room temperature before testing.

258 Differential scanning calorimetry (DSC, Supplementary Figure S2) indicated that the
259 majority of volatiles in the CMS are lost in the drying stage of sample preparation. A
260 broad melting peak was evident in the dried and burnt samples between 20 and 40°C,
261 with a sharp exothermic peak at 20°C on cooling, which is attributed to the fat phase.

262 The effect of temperature on the fat component was evaluated by studying the rheology
263 of the emulsion employed in the formulation over the range 10-60°C, spanning the
264 temperatures employed in the cleaning tests. The fat present in the soil contains less
265 water and its rheological behaviour will be affected by changes introduced by baking
266 and components absorbed from other ingredients in the CMS, so these results are
267 interpreted as indicators of the fat behaviour. Samples were tested in a Malvern Kinexus
268 rheometer using a 40 mm diameter smooth 4° cone and plate configuration. Shear rate
269 sweeps at 22°C indicated viscoplastic behaviour (see Supplementary Figure S3 inset)
270 with a critical stress of approximately 160 Pa and a critical shear rate of around 1 s⁻¹.
271 Measurement of apparent viscosity were therefore made at 0.1 s⁻¹ at intervals of 5 K.
272 The apparent viscosity decreased strongly with temperature until 40°C, above which it
273 was almost insensitive to temperature and the behaviour was Newtonian. This was

274 interpreted as the temperature at which the fat phase in the soil was expected to become
275 mobile (i.e. more free flowing). These observations are consistent with the DSC results.

276 The substrates were fabricated from 316 stainless steel. The data presented here were
277 obtained using 50 mm square plates with thickness 3 mm and surface root mean square
278 roughness, $R_q = 1.6 \mu\text{m}$ (measured using a scanning confocal thickness sensor, Micro-
279 Epsilon model IFS2405-3). Prior to applying the soil the substrates were cleaned by
280 sonication for 10 minute periods in aqueous 1M NaOH, dishwashing solution (Fairy
281 LiquidTM in reverse osmosis water, $< 5 \text{ g L}^{-1}$) then acetone, scrubbing with a soft cloth
282 following each sonication step. Cleaning was repeated if any residual soil was visible.
283 After each test any remaining soil was removed using a plastic spatula and the plate left
284 to soak in 1M NaOH/soap solution overnight and rinsed with deionised water before
285 undergoing the procedure outlined above.

286 Figure 1 shows photographs of the soil layer before and after baking. Drying was
287 accompanied by a loss of around 50 % of the initial soil mass, which is comparable
288 with the water content of the mixture (Table 1). A further 10 wt.% was lost during
289 baking and was accompanied by visible cracking of the layer (see Figure 1(b)). It was
290 not possible to generate layers of this soil free from cracks but prolonging the drying
291 time, such as allowing the moisture to evaporate overnight before baking, reduced the
292 severity and size of the cracking. Thinner soiling layers ($\delta_{\text{initial}} < 200 \mu\text{m}$) exhibited
293 finer scale cracking patterns, as defined both by cracking frequency and width, than
294 thicker ones ($\delta_{\text{initial}} > 500 \mu\text{m}$), which is consistent with the literature on film cracking
295 (Lee and Routh, 2004).

296 The crack pattern structure was quantified using two methods. The first was based on
297 the fraction of the plate area occupied by cracks. This was calculated by converting a
298 photograph into a binary image in MatlabTM (Figure 1(c)) and dividing the soiled region
299 into ten equal strips. The fraction of cracked area was calculated for each strip, giving
300 an average of 38.8% with a standard deviation of 5.3%. The second was to count the
301 number of cracks along 9 equally-spaced gridlines (Figure 1(d)). This gave averages (\pm
302 standard deviation) in the vertical and horizontal directions of 19.0 ± 3.0 and $21.2 \pm$
303 2.6 , respectively, corresponding to a crack spacing of approximately 2.5 mm.

304

305 *Millimanipulation flow system*

306 The millimanipulation device described by Magens *et al.* (2017) (Figure 2) was
307 modified to include a solution circulation system. The sample is located on a computer-
308 controlled translation stage (labelled E on the figure, Standa 103880) which moves the
309 sample so that the layer is forced against the blade (B, 24.6 mm long) at set velocity V .
310 The blade is mounted on the end of a frictionless pivot and the force imposed on the
311 blade is measured by a force transducer (C). Upwards motion of the blade, which would
312 affect the measurement, is inhibited by a counterweight (D). Further details of the
313 device and its operation are given in Magens *et al.* (2017).

314 The sample mount is located within a stainless steel chamber (internal dimensions
315 113×61×13 mm). The volume of solution volume held in the chamber after locating the
316 sample is approximately 87 ml.

317 A stirred 1 litre jacketed vessel served as the solution reservoir. Liquid is delivered at a
318 set flow rate by a peristaltic pump to the base of the sample chamber (marked I). The
319 solution passes across the chamber and leaves via the outlet located on the far wall
320 before draining back to the reservoir under gravity. The reservoir contents are heated
321 by recirculation of hot water through the jacket. The temperature of the solution is
322 monitored by a thermocouple located in the sample chamber. Changes to solution
323 composition are made in the reservoir.

324 The tests reported here featured a solution flow rate of 100 ml min^{-1} , giving a space
325 time of approximately 53 s. The time taken for a change in solution chemistry to take
326 effect in the chamber was determined by a simple residence time test whereby the
327 conductivity of the solution in the reservoir was altered by adding a 10 mL dose of 1 M
328 NaOH and monitoring the conductivity of the liquid leaving the chamber. Figure 3
329 shows that breakthrough is observed after approximately 30 seconds followed by a two-
330 step change in conductivity which could be modelled approximately as plug flow (along
331 the connecting tubing) in parallel with a mixing element. The inset in Figure 3 shows
332 that the change in conductivity was complete after 150 s at this flow rate.

333

334 *Test protocol*

335 Cleaning solution was initially circulated through the empty chamber to bring it to the
336 required temperature. The solution was allowed to drain and the sample swiftly
337 mounted in place, dry, and the millimanipulation blade located to pass over the substrate
338 with a 50 μm gap. Solution was then reintroduced and pumped through the chamber at
339 a rate of 100 ml min^{-1} . Once the surface of the layer was immersed, the blade motion
340 was initiated. The blade moved across the sample at velocity V for a set time t_s to give
341 a total displacement $X = Vt_s$. The velocity and distance travelled can be set as required
342 (see Magens *et al.*, 2017). In these tests V was 0.1 mm s^{-1} and the force on the blade was
343 recorded at 151 Hz. For ease of plotting, the data are truncated on a 1:100 basis. The
344 removal force per unit width, F_w , was calculated from

$$345 \quad F_w = \frac{\text{measured force}}{\text{blade width}} \quad [1]$$

346 Tests were performed in triplicate. Removal profiles such as Figure 6 feature the
347 average value of F_w plotted against blade-soil displacement, x . Later profiles show F_w
348 plotted against time in contact with cleaning solution: since V is constant in these tests,
349 the abscissa is readily converted between x and t .

350 Interpretation of F_w measurements in terms of material parameters and relating these to
351 cleaning applications requires some care, as outlined by Ali *et al.* (2015b). When
352 removal occurs purely by adhesive failure, F_w provides a measure of the work required
353 to peel a deposit away from a surface and this can be related to forces (or momentum)
354 applied to a layer by a tool or a flow. When removal occurs by cohesive breakdown, a
355 quantitative model of the deformation is needed to isolate the contributions from
356 rheological parameters such as yield strength and elastic compression to the measured
357 force. These material parameters then need to be compared with the forces imposed in
358 the cleaning operation. For cleaning in pipe flows, these are typically related to fluid
359 shear but in cleaning by impinging jets or liquid films, shear and extensional forces can
360 act depending on the geometry and whether the liquid film is confined or has a free
361 surface. At a coarse level, F_w can be used to gauge the change in material strength.

362 *Test solutions*

363 Tests solutions were prepared in batches using 1 L deionised water and the pH adjusted
364 to 7, 9 or 12 using 1 M aqueous NaOH. Surfactant solutions were prepared at 1 wt.%

365 loading using sodium dodecyl benzene sulfonate (SDBS, anionic, critical micelle
366 concentration (CMC) 0.1 g L^{-1} (Sanz *et al.* 2003), hexadecyltrimethylammonium
367 bromide (CTAB, cationic, CMC 0.334 g L^{-1} (Previdello *et al.* 2006), and t-
368 octylphenoxypolyethoxyethanol (TX-100, non-ionic; CMC 0.0131 g L^{-1} (Ruiz *et al.*
369 2001). The mixtures were prepared by stirring at $50 \text{ }^\circ\text{C}$ for 30 minutes before being left
370 to cool to room temperature.

371

372 **Results and Discussion**

373 *Effect of contact with cleaning solution for set time*

374 The impact of immersion was initially assessed by comparing F_w before and after the
375 sample was contacted with cleaning solution for a set time. Dry samples prepared on
376 discs or square plates were mounted in the solution chamber with no liquid present and
377 F_w measured at $V = 0.1 \text{ mm s}^{-1}$ for 200 s, giving $X_{\text{dry}} = 20 \text{ mm}$ (region A in Figure 4).
378 Solution was then introduced to the chamber for periods ranging from 1 - 60 min with
379 the sample stationary, after which F_w was measured for a further 200 s, giving 20 mm
380 $< X_{\text{wet}} \leq 40 \text{ mm}$. A section of undisturbed material 10 mm long remained. Figure 4(b)
381 shows an example of a square plate following testing with 1 wt% SDBS solution at pH
382 10 and room temperature. There is a noticeable amount of residual material on the
383 substrate in region A (dry removal) compared with region B (following soaking),
384 indicating that the adhesion of the soil to the substrate had decreased significantly.

385 The change in soil behaviour was also evident in the behaviour of the removed oil.
386 Figure 5(a) shows that, prior to soaking, removal is characterised by the ‘chipping’
387 away of small chunks of material by the blade. After soaking, the removed soil forms
388 a weakly cohesively-bound heap ahead of blade (Figure 5(b)). The absence of much
389 residual material on the substrate indicates that adhesion of the soil layer was reduced
390 more than cohesive interactions within the layer.

391 The importance of mechanical action is demonstrated by the presence of the residual
392 material in region A and the original soil layer in region C. These remained in place,
393 unchanged, after soaking, indicating that the weak shear force associated with the
394 solution flow was not large enough to disrupt either material.

395 The corresponding F_w profiles are shown in Figure 6. The dry profiles exhibit a cut-off
396 at 430 N m^{-1} , which is due to the maximum force that could be measured for this setting
397 of the transducer. The range can be extended by adjusting the transducer position, at
398 the expense of reducing the sensitivity for weaker layers. The oscillations evident in the
399 dry F_w profiles arise from the cracked nature of the soils. Regions free of deposit do not
400 contribute to the force on the blade, and the periodicity is roughly consistent with the
401 average measured crack spacing of 2.3 mm (Figure 1(d)). The average value of F_w for
402 dry samples was consistent between tests, at approximately 400 N m^{-1} (1 s.f.). This is
403 comparable with the F_w values reported by Ali *et al.* (2015b) for baked lard (up to 430
404 N m^{-1} for oils cooked for 5 hr at 220°C).

405 The F_w profiles for samples soaked at pH 10 at room temperature in Figure 6(b) show
406 similar oscillation, associated with inhomogeneous coverage, and a general reduction
407 in absolute amplitude with time. The relative amplitude of oscillation is consistent at
408 approximately 20 % of the mean F_w value indicating the impact of the cracking is
409 consistent over the test duration. The values are larger than those reported by Akhtar
410 *et al.* (2010) and Bobe *et al.* (2007) of 0.1 - 0.3 and 1.3 N m^{-1} for fresh caramel and
411 yeast layers, respectively. With extended soaking they approach those reported by Ali
412 *et al.* (2015b) for unbaked oil soils with thickness ranging from 0.3 to 0.6 mm, of 0-20
413 N m^{-1} .

414 The average F_w value is plotted against soaking time in Figure 7, normalised by the dry
415 value. After 10 minutes of soaking there was virtually no variation in F_w . Much of the
416 weakening of the adhesive forces occurred within the first 10 minutes of soaking, and
417 there is a noticeable reduction in F_w for the test started after 5 minutes of soaking,
418 indicating that changes were occurring over this timescale. Subsequent testing focused
419 on shorter soaking periods, measuring F_w continuously for 500 s after the soil contacted
420 the solution.

421 Figure 7 also shows the average F_w values measured after soaking in 1 wt% SDBS
422 solution at the same temperature and pH. There is no significant effect of this anionic
423 surfactant, as both data sets exhibit an almost exponential decay to $F_{w,\text{wet}}/F_{w,\text{dry}} = 0.05$
424 after 10 minutes. The F_w value obtained with SDBS after 60 minutes was larger than at
425 10 minutes, which was attributed to this sample having swollen more and having

426 absorbed more water. Similar results were obtained for SDBS solutions at pH 11 and
427 12 (data not reported).

428

429 *Effect of contact with solution, continuous measurement: effect of temperature*

430 Figure 8(a) shows examples of removal profiles obtained with no pre-soaking in water
431 at pH 7 and 20 °C, with no surfactant present. The initial F_w values are noticeably
432 smaller than the average of 400 N m^{-1} for dry deposits evident in Figure 6(a). This arises
433 from the nature of the layer at the edge of plates differing from that in the interior. When
434 the slurry is applied to the plate the layer is pinned at the edges so the layer thickness
435 is thinner there and subject to a different drying and baking history. Data obtained for t
436 $< 40 \text{ s}$ (labelled A on the Figure) and $t > 460 \text{ s}$ (labelled D) were therefore excluded
437 from comparisons.

438 It is evident that stage A masks a rapid reduction in removal force caused by hydration
439 following initial contact with solution. The F_w values measured after 60 s (stage B) lie
440 in the range $100 - 150 \text{ N m}^{-1}$, which is larger than that observed at pH 10 (Figure 6):
441 the effect of pH is discussed in the next section. In stage B there is a slow decrease in
442 F_w with time which in Figure 8(a) is masked by the scatter in the data: this feature is
443 clearer in Figure 8(b), obtained at 50°C, and subsequent plots.

444 After 460 s at 20°C, there is a transition to a faster decay in F_w (labelled stage C): the
445 transition time is labelled t_c . At 50°C, Figure 8(b), $t_c \sim 220 \text{ s}$ and F_w decreases more
446 quickly, with noticeably less scatter. The data could be fitted to an exponential decay
447 expression with characteristic decay time, D , $\sim 125 \pm 3 \text{ s}$, as well as less scatter.

448 The photographs in Figure 8 show that the transition is accompanied by a change in the
449 amount of soil remaining on the substrate, with almost no residual material after t_c .
450 These findings indicate that the adhesion of the soil to the substrate changes at t_c : the
451 soil is still removed as a coherent layer, with cohesion within the soil (which may be
452 decreasing due to the uptake of water) stronger than the adhesion to the substrate.

453 The B/C transition is more likely to arise from water penetrating through the soil (*i.e.*
454 related to absorption and diffusion) rather than being due to ingress of water at the soil-

455 substrate interface. The latter would start as soon as there was contact with solution via
456 the network of cracks in the layer.

457 Figure 8 confirms that temperature is an important parameter in cleaning of the CMS
458 material, as Sinner's circle indicates. 50°C is a standard operating temperature in
459 domestic dishwashers, and lies above the temperature estimated for the fat-rich phase
460 in the CMS to become more fluid. The time taken for a 200 µm thick soil layer to reach
461 50°C after contacting the solution can be estimated by considering conduction through
462 a slab of baked material with a thermal diffusivity of $2 \times 10^{-7} \text{ m}^2/\text{s}$ (Rask, 1989). This
463 gives a heating time of order 1 s, which is negligible. The initial F_w values are larger at
464 50°C than at 20°C (but subject to considerable scatter), which may be due to faster
465 swelling. The B/C transition occurs earlier, which is consistent with faster diffusion,
466 while the presence of mobile fat is likely to facilitate adhesive failure. A pseudo-
467 exponential decay in stage C was not observed at 20° C. This may be because the
468 solution was not in contact with the solution for long enough at this lower temperature.

469

470 *Effect of pH*

471 Many detergents are alkaline as this promotes swelling of proteins and hydrolysis of
472 fats. The impact of pH on removing CMS layers was investigated primarily with water
473 at pH 7 and aqueous NaOH solutions (pH 9 and 12) at 20 °C and at 50 °C.

474 Figure 9 shows that pH had little influence at 20 °C. The removal profiles are similar,
475 with initial F_w values following hydration between 140 and 200 N m^{-1} , followed by a
476 slow linear decay. The B/C transition evident at pH 7 was not observed at pH 9 and
477 occurred later, around 410 s, at pH 12. As a result the non-edge data were fitted to a
478 simple linear trend: the decay rate was greatest at pH 9.

479 The removal profiles at 50°C at pH 9 and pH 12 in Figure 10 do not show the marked
480 transition evident at 220 s at pH 7 (Figure 8(b)). Decay profiles measured at pH 6 and
481 8 were similar to those at pH 7 (Supplementary Figure S4). The initial F_w values are
482 similar to those at 20 °C and the linear decay rates were faster at this higher temperature,
483 at $0.51 \pm 0.01 \text{ N m}^{-1} \text{ s}^{-1}$ (pH 7) and $0.26 \pm 0.01 \text{ N m}^{-1} \text{ s}^{-1}$ at pH 9 and 12. Whereas F_w
484 decayed almost exponentially in stage C at pH 7, the decay at pH 9 is close to linear

485 until $t \sim 420$ s and at pH 12 F_w does not decay strongly until around 300 s. The
486 photograph provided as insets show a gradual change in residual soil on the substrate,
487 which is consistent with the removal profiles.

488 The effect of alkali at 50°C is unexpected, as higher pH often accelerates cleaning of
489 proteinaceous food soils (Morison and Thorpe, 2002; Fryer and Asteriadou, 2009),
490 although some proteinaceous soils exhibit an optimal pH in alkaline cleaning (Mercade-
491 Prieto *et al.*, 2006). In the absence of surfactants the cleaning agents active in this case
492 are water (hydrating starch and proteins, dissolving soluble components), hydroxyl ions
493 (indicative of pH) and Na^+ counterions (both of which contribute to ionic
494 strength/osmotic effects). Alkali conditions are known to cause unbaked protein layers
495 to swell and promote erosion at the soil-solution interface (Tuladhar *et al.*, 2000;
496 Christian and Fryer, 2006). Swelling would be expected to enhance transport of water
497 to the substrate/soil interface and weaken the soil adhesion. Similarly, Otto *et al.* (2016)
498 reported that unbaked starch deposits are expected to become more negatively charged
499 at high pH and therefore be repelled from stainless steel surfaces which are similarly
500 charged under these condition (isoelectric points typically pH 4-5 for 304 stainless steel
501 (Lefevre *et al.*, 2009) and 5.1 for starch from wheat flowers (Kemp, 1936).

502 The results indicate that the hydroxyl ions are retarding the weakening of the adhesive
503 interactions, which could be due to hydrolysis of the fats or inhibiting the mobility of
504 the mobile fat phase, thereby retarding the access of water to the soil-substrate interface.
505 The material at the interface is a complex mixture which has been subject to the oven
506 temperature for 7 minutes (as a result of fast conduction through the steel). Further work
507 is required to identify the components and processes active at this interface.

508 *Effect of surfactant*

509 The effect of 1 wt% surfactant was studied at pH 9 at 20°C and 50°C, representing
510 standard dishwasher operating conditions. Figure 11 shows that the non-ionic (TX-100)
511 and anionic (SDBS) surfactants gave no enhancement in removal, with similar changes
512 in F_w over the test period (linear decay rates of $0.14\text{-}0.15 \pm 0.01 \text{ N m}^{-1} \text{ s}^{-1}$). This is
513 consistent with Figure 7 (pH 10 and 20 °C). Detry (2007, 2009) and Bobe (2007)
514 demonstrated a beneficial impact of LAS-type surfactant in similar conditions on
515 unburnt soils. This finding could be explained by the LAS acting via an

516 erosive/emulsification cleaning mechanism. Erosive cleaning has been shown by
517 Gillham *et al.* (1999) and Chen *et al.* (2012) to be less effective for burnt materials due
518 to their increased cohesive strengths and cross-linked polymeric structures relative to
519 their unburnt counterparts.

520 In contrast the cationic agent, CTAB had immediate impact, giving almost exponential
521 decay behaviour (initial decay rate $0.42 \pm 0.01 \text{ N m}^{-1} \text{ s}^{-1}$), similar to pH 7 at 50°C, but
522 without an evident B/C transition. The latter transition could have occurred at $t < 40 \text{ s}$,
523 suggesting that either (i) CTAB aided the penetration of water through the soil to the
524 substrate, or (ii) the reduction in adhesion was caused by ingress at the soil-substrate
525 interface via the many cracks present in the soil layer. The photograph of the cleared
526 region shows little residual material on the substrate, confirming that CTAB had
527 promoted adhesive failure. The ability of CTAB to promote removal at room
528 temperature brings immediate advantages in terms of energy consumption.

529 Figure 12 shows that all three surfactants promoted removal at 50°C at pH 9 compared
530 to a simple alkaline solution. The removal profile for CTAB (Figure 12(a)) is similar
531 to that at 20°C: fitting the data sets to simple exponential decay relationships gave $D =$
532 $213 \pm 4 \text{ s}$ and $238 \pm 5 \text{ s}$ at 20°C and 50°C, respectively. Temperature does not appear
533 to have affected the CTAB mechanism. Determining the mechanism involved requires
534 further work, but two possible explanations are (i) the cationic surfactant being attracted
535 to the negatively charged starch-based moieties within the soil at pH 9; and (ii) the
536 cationic surfactant having greater affinity for the stainless steel surface (which acquires
537 a negative charge at pH 9), disrupting the adhesive bonding between the soil and the
538 substrate at the interface and therefore lowering F_w even at room temperature.
539 Hypothesis (ii) could be tested by using substrates with a different IEP but similar
540 surface energy and heat conduction properties. In practice, hypothesis (ii) suggests that
541 the effectiveness of a CTAB-based formulation would vary between surfaces.

542 The removal profiles for TX-100 and SDBS are both similar to that for water at pH 7
543 (Figure 8(b)), but with earlier B/C transition: t_c for TX-100 is markedly shorter, at
544 approximately 80 s, while F_w decays more rapidly than with CTAB, with $D = 139 \pm 3$
545 s. SDBS behaviour is very similar to the surfactant-free solution until $t_c = 200 \text{ s}$, after
546 which F_w decays exponentially, unlike the alkaline solution, with $D = 120 \pm 3 \text{ s}$. The

547 final F_w values for TX-100 and SDBS (*i.e.* at $t = 460$ s) are both smaller than that
548 observed with CTAB.

549 The decay behaviours and decay rate parameters are summarised in Table 2. The
550 existence of the B/C transition, faster decays and lower final F_w values all indicate that
551 a different mechanism is involved in softening of the soil layer by the non-ionic and
552 anionic surfactants.

553 The reason why TX-100 and SDBS promote behaviour observed at pH 7, essentially
554 inhibiting the effect of higher pH, is now considered. SDBS will increase the solution
555 ionic strength, while TX-100 will have little effect on charge. The observation that these
556 surfactants are not effective at 20°C, when the fat phase is immobile, indicates that the
557 mechanism is linked to the solubilising of fat globules present in the soil. Non-ionic
558 surfactants are known to be effective at removing oily soils from synthetic fibres
559 (Williams, 2007), whereas anionic surfactants are effective at removing (positively
560 charged) particles. Since the fat prevents the ingress of water through the soil matrix,
561 agents which promote the removal of this phase will enhance penetration of water and
562 hydration at the soil-substrate interface. Removal of the oil phase will also affect the
563 rheology of the hydrated soil, which will be manifested in the cohesive contribution to
564 the force measured by the millimanipulation blade. This mechanism would not be
565 directly affected by the nature of the substrate to the same degree as that promoted by
566 CTAB. The substrate would have an indirect effect in terms of wetting characteristics
567 towards components in the soil, heat transfer etc. and therefore microstructure of the
568 fouling layer at the soil-substrate interface (see Magens *et al.*, 2017).

569 These results demonstrate how the different agents effect cleaning, reducing the
570 strength of the soil at the soil-substrate interface via different mechanisms. The same
571 length of time may be required to remove the CMS layers studied here from a stainless
572 steel surface, but knowledge of the mechanisms – whether ingress or penetration –
573 allows one to gauge whether or not the agent will give similar efficacy for other soils
574 on different substrates.

575 The cleaning mechanism and behaviour is ultimately determined by the nature and
576 microstructure of the soil. For example, Ali *et al.* (2015a) studied the cleaning of
577 polymerised lard soil layers on stainless steel and reported that solutions of TX-100 and
578 LAS at pH 10.4-11 promoted solution ingress and soil detachment at the soil-substrate

579 interface, while CTAB promoted penetration through the soil layer (rather than
580 promoting ingress as observed in this work). These differences illustrate how, like
581 coatings to prevent deposition and fouling, detergent solutions need to be matched to
582 the soil.

583

584 **Conclusions**

585 The millimanipulation technique has been extended to allow the forces at the soil-
586 substrate interface to be measured whilst being immersed and soaked in cleaning
587 solutions in real time. The complex model food soil tested comprised burnt fats, starch
588 and proteins in a cracked layer on stainless steel: it was not possible to prepare uniform
589 soil layers. The adhesion forces decreased noticeably on hydration.

590 The soils exhibited cohesive or adhesive failure during removal, depending on the
591 cleaning solution chemistry. Temperature had a uniformly beneficial effect on cleaning,
592 with water at pH 7 at 50°C exhibiting a transition between cohesive and adhesive failure
593 after an initial soaking period. The length of this initial soaking period was reduced
594 when TX-100 or SDBS was present. This behaviour is attributed to the fat in the soil
595 being mobile at 50°C. CTAB, the cationic surfactant, promoted adhesive failure at 20°C
596 and 50°C, indicating that its action involved a different mechanism.

597 The pH of the solution impacts had little influence at 20 °C. At 50 °C, high pH gave
598 slower cleaning than at pH 6-8, even though alkaline conditions are expected to
599 promote swelling and weakening of proteins in the deposit. All three surfactants studied
600 promoted removal at high pH, with TX-100 giving greatest reduction in soil strength.
601 The results provide quantitative evidence that different cleaning mechanisms are
602 promoted by the different cleaning agents, and allow their role in Sinner's circle to be
603 quantified in terms of the extent and rate of change of the rheology of the soil at the
604 soil-substrate interface.

605

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609

610 **Open Data**

611 The data presented in this study are available from the University of Cambridge's

612 Apollo data repository at doi [10.17863/CAM.26373](https://doi.org/10.17863/CAM.26373).

613 **References**

- 614 Akhtar, N., Bowen, J., Asteriadou, K., Robbins, P. T., Zhang, Z., Fryer P. J. (2010)
615 Matching the nano- to the meso-scale: Measuring deposit–surface interactions
616 with atomic force microscopy and micromanipulation, *Food and Bioproducts*
617 *Processing*, 88, 341–348.
- 618 Ali, A. (2015) PhD: Understanding the cleaning of greasy polymerised food soils.
619 University of Cambridge, Cambridge.
- 620 Ali, A., Alam, Z., Ward, G., Wilson, D. I. (2015a) Using the fluid dynamic gauging
621 device to understand the cleaning of baked lard soiling layers. *J. Surfactants*
622 *Detergents*, 18, 933-947.
- 623 Ali, A., de’Ath, D., Gibson, D., Parkin, J., Ward, G., Alam, Z. and Wilson, D.I. (2015b)
624 Development of a millimanipulation device to quantify the strength of food
625 fouling deposits, *Food Bioproducts Proc.*, 93, 265-258
- 626 Asteriadou, K., Othman, A.M., Goode, K., Fryer, P.. (2009) Improving cleaning of
627 industrial heat induced food and beverages deposits: A scientific approach to
628 practice. *Heating Exchanger and Fouling Conference*. 158-164
- 629 Ashokkumar, S., Adler-Nissen, J., 2011. Evaluating non-stick properties of different
630 surface materials for contact frying. *J. Food Eng.* 105, 537–544.
- 631 Basso, M., Simonato, M., Furlanetto, R., De Nardo L., (2017) Study of chemical
632 environments for washing and descaling of food processing appliances: An
633 insight in commercial cleaning products. *J. Ind. Eng. Chem.*, 53, 23-36.
- 634 Bishop, A. 1997, *Cleaning in the Food Industry*, Reprinted by permission of Wesmar
635 Company Inc. from *Basic Principles of Sanitation*.
- 636 Bobe, U., Hofmann, J., Sommer, K., Beck, U., Reiners, G., (2007) Adhesion - where
637 cleaning starts, *Trends Food Sci. Technol.*, 18, 36-39.
- 638 Castner, D. G., Ratner, B. D. (2002) Biomedical surface science: foundations to
639 frontiers. *Surf. Sci.*, 500, 28-60.
- 640 Chen, X., Fickak, A., Hatfield, E. (2012) Influence of run time and aging on fouling
641 and cleaning of whey protein deposits on heat exchanger surface. *J. Food Res.*,
642 1, 212-224.
- 643 Chew, J.Y.M., Paterson, W.R. and Wilson, D.I. (2004) Dynamic gauging for measuring
644 the strength of soft deposits, *J. Food Eng.* 65(2), 175-187.
- 645 Christian, G. K., Fryer, P. J. (2006) The effect of pulsing cleaning chemicals on the
646 cleaning of whey protein deposits, *Food Bioproducts Proc.*, 84, 320-328.

- 647 Detry J. G., Rouxhet, P. G., Boulange-Petermann, L., Deroanne, C., Sindic, M., (2007)
648 Cleanability assessment of model solid surfaces with a radial-flow cell. *Colloids*
649 *Surf. A: Physicochem. Eng. Aspects*, 302, 540-548.
- 650 Detry, J. G., Deroanne, C., Sindic, M. (2009) Hydrodynamic systems for assessing
651 surface fouling, soil adherence and cleaning in laboratory installations,
652 *Biotechnol. Agron. Soc. Environ.* 13, 427-439
- 653 Din, R. A., Bird, M. R. (1996) The effect of water on removing starch deposits formed
654 during baking, *Proc. 2nd European Conference for Young Researchers in*
655 *Chemical Engineering, Leeds, UK*, 1, 187-189.
- 656 Dunstan, T. S., Fletcher, P. D. I., (2014) The removal of thermally aged films of
657 triacylglycerides by surfactant solutions. *J. Surfact. Deterg.*, 17, 899-910.
- 658 Fryer, P. J., Asteriadou, K. (2009) A prototype cleaning map: a classification of
659 industrial cleaning processes. *Trends in Food Science & Technology*, 20, 225-
660 262.
- 661 Gordon, P.W., Brooker, A.D.M., Chew, Y.M.J., Wilson, D.I., York, D.W. (2010)
662 Studies into the swelling of gelatine films using a scanning fluid dynamic gauge,
663 *Food & Bioprod. Proc.*, 88, 357-364
- 664 Gillham, C. R., Fryer, P. J., Hasting, A. P. M. and Wilson, D. I. (1999) Cleaning-in-
665 place of whey protein fouling deposits: Mechanisms controlling cleaning,
666 *Food Bioprod. Proc.*, 77, 127-136.
- 667 Gillham, C.R., Fryer, P.J., Hasting, A.P.M. and Wilson, D.I. (2000) Enhanced cleaning
668 of whey protein fouling deposits using pulsed flows, *J. Food Engineering*, 46(3),
669 199-209.
- 670 Hauser, G. (2008) *Hygiene gerechte Apparate und Anlagen: für die Lebensmittel-,*
671 *Pharma- und Kosmetikindustrie.* Wiley-VCH, Weinheim
- 672 Israelachvili, J. (2011) *Intermolecular and Surface Forces*, Elsevier. Ch. 13, 17.
- 673 Jennings, W. G., (1965) Theory and practice of hard-surface cleaning, *Adv. Food Res.*,
674 14, 325-458
- 675 Jonhed, A., Andersson, C., Jarnstrom, L. (2008) Effects of film forming and
676 hydrophobic properties of starches on surface sized packaging paper. *Packaging*
677 *Technol. Sci.*, 21, 123-135.
- 678 Jurado-Alameda, E., Herrera-Márquez, O., Martínez-Gallegos, J. F., Vicaria, J. M.
679 (2015) Starch-soiled stainless steel cleaning using surfactants and α -amylase, *J.*
680 *Food Eng.* 160, 56-64.

- 681 Kemp, I. (1936) The surface analysis of particles of certain wheat flours. *Trans. Faraday*
682 *Soc.*, 32, 837-843.
- 683 Kumar, A., Staedler, T., Jiang, X. (2013) Role of relative size of asperities and adhering
684 particles on the adhesion force. *J. Colloid Interface Sci.* 409, 211-218.
- 685 LaMarche, C., Leadley, S., Liu, P., Kellogg, K.M., Hrenya, C.M., (2017) Method
686 of quantifying surface roughness for accurate adhesive force predictions,
687 *Chem. Eng. Sci.*, 158, 140-153.
- 688 Lee, W.P., Routh, A.F. (2004) Why do drying films crack? *Langmuir*, 20, 9885-9888.
- 689 Lefèvre, G., Čerović, L, Milonjić, S., Fédoroff, M., Finne, J., Jaubertie, A. (2009)
690 Determination of isoelectric points of metals and metallic alloys by adhesion of
691 latex particles, *J. Colloid Interface Sci.*, 337, 449–455.
- 692 Lelièvre, C., Legentilhomme, P., Gaucher, C., Legrand, J., Faille, C., and Bénézech,
693 T. (2002) Cleaning in place: Effect of local shear stress variation on bacterial
694 removal from stainless steel equipment, *Chem. Eng. Sci.*, 57, 1287–1287.
- 695 Lelieveld, H.L.M., Mostert, M.S., Holah, J. (2005) Handbook of hygiene control in the
696 food industry. EHEDG, Cambridge, UK, publ. Woodhead, 192 – 208.
- 697 Li, H., Koutzenko, B., Chen, X.D., Jentet, R., Mercadé-Prieto, R. (2015) Cleaning
698 beyond whey protein gels: Egg white, *Food Bioproduct Proc.*, 93, 249-255.
- 699 Liu, W., Christian, G. K., Zhang, Z., Fryer, P.J. (2002) Development and use of a
700 micromanipulation technique for measuring the force required to disrupt and
701 remove fouling deposits. *Food Bioprod. Proc.* 80, 286-291.
- 702 Liu, W., Fryer, P.J., Zhang, Z., Zhao, Q., Liu, Y. (2006) Identification of cohesive and
703 adhesive effects in the cleaning of food fouling deposits. *Innovative Food*
704 *Science Emerging Tech.*, 7, 263-269.
- 705 Magens, O.M., Liu, Y., Hofmans, J.F.A., Nelissen, J.A., Wilson, D.I. (2017)
706 Adhesion and cleaning of foods with complex structure: Effect of oil content
707 and fluoropolymer coating characteristics on the detachment of cake from
708 baking surfaces, *J. Food Eng.*, 197, 48-59.
- 709 Mashmouhy, H., Zhang, Z., Thomas, C.R., (1998) Micromanipulation measurement
710 of the mechanical properties of baker's yeast cells, *Biotechnology Techniques*,
711 12, 925–929.

- 712 Mauermann, M., Eschenhagen, U., Bley T. H., Majschak, J.-P. (2009) Surface
713 modifications e Application potential for the reduction of cleaning costs in the
714 food processing industry, Trends Food Science & Technology, 20, 8-15
- 715 Mercadé-Prieto, R., Falconer, R.J., Paterson, W.R., Wilson, D.I. (2006) Probing the
716 mechanisms limiting dissolution of whey protein gels during cleaning, 84, 311-
717 319
- 718 Moeller, R. S., Nirschl, H. (2017) Adhesion and cleanability of surfaces in the baker's
719 trade, J. Food Eng., 194, 99-108.
- 720 Morison, K. R., Thorpe, R. J. (2002) Spinning disc cleaning of skimmed milk and whey
721 protein deposits. Food Bioprod. Proc, 80, 319-325.
- 722 Otto, C., Zahn, S., Hauschild, M., Babick, F., Rohm, H. (2016) Comparative cleaning
723 tests with modified protein and starch residues, J. Food Eng. 178, 145-150.
- 724 Palmisano, P., Hernandez, S. P., Hussaina, M., Finoa, D., Russoa, N. (2011) A new
725 concept for a self-cleaning household oven, Chem. Eng. J, 176–177, 253–259.
- 726 Pérez-Mohedano, R., Letzelter, N., Bakalis, S. (2016) Swelling and hydration studies
727 on egg yolk samples via scanning fluid dynamic gauge and gravimetric tests. J.
728 Food Eng., 169, 101-113.
- 729 Pongsawasdi, P., Murakami, S. (2010) *Carbohydrases in detergents*, Nova Science
730 Publishers, 71-95.
- 731 Previdello B. A. F., Carvalho F. R. D., Tessaro A. L., Souza V. R. D., and Hioka N.,
732 (2006). The pKa of acid-base indicators and the influence of colloidal systems.
733 Química Nova, 29, 600–606.
- 734 Prochaska, K., Kędziora, P., Thanh, J.L., Lewandowicz, G. (2007) Surface activity of
735 commercial food grade modified starches. Coll. Surf. B. Biointerfaces, 60, 187-
736 194.
- 737 Rask, C. (1989) Thermal properties of dough and bakery products: A review of
738 published data, J. Food Eng, 9, 167-193.
- 739 Rosa, F., Roviada, E., Graziosi, S., Giudici, P., Guarnaschelli, C., and Bongini, D. (2012)
740 Dishwasher history and its role in modern design, Third IEEE History of
741 Electro-technology conference 'The Origins of Electrotechnologies', Pavia,
742 Italy.
- 743 Rosen, M. J., Kunjappu, J.T, 2012, *Surfactants and Interfacial Phenomena*, John
744 Wiley & Sons Inc., New Jersey, 2012.

- 745 Ruiz C. C., Molina-Bolivar J. A., Aguiar J., MacIsaac G., Moroze S., and Palepu R.,
746 (2001). Thermodynamic and structural studies of Triton X-100 micelles in
747 ethylene glycol-water mixed solvents. *Langmuir*, 17, 6831–6840.
- 748 Saikhwan, P., Mercadé-Prieto R., Chew , Y.M.J., Gunasekaran, S., Paterson, W.R. and
749 Wilson, D.I. (2010) Swelling and dissolution in cleaning of whey protein gels,
750 *Food & Bioproducts Proc.*, 88, 375–383.
- 751 Sanz J., Lombraña J. I., and Luís A.de, (2003). Ultraviolet-H₂O₂ oxidation of
752 surfactants. *Environmental Chemistry Letters*, 1, 32–37.
- 753 Showell, M., 2005, Part D: Formulation, *Handbook of Detergents*, Boca Raton, Florida,
754 CRC Press, 158-163.
- 755 Stanga, M., (2010) *Sanitation: Cleaning and Disinfection in the Food Industry*.
756 Wiley VCH, Weinheim.
- 757 Tuladhar, T. R., Paterson, W. R., Wilson, D. I. (2002) Thermal conductivity of whey
758 protein film undergoing swelling: measurement by dynamic gauging, *Food*
759 *Bioprod. Proc.*, 80, 332-339.
- 760 Williams, J, (2007), Formulation of Carpet Cleaners, *Handbook for Cleaning /*
761 *Decontamination of Surfaces*, 1, 103-123.
- 762

763 **Nomenclature**

764 **Roman**

765	D	characteristic decay time (s)
766	h	height of blade above substrate (m)
767	F_w	removal force per unit width (N m^{-1})
768	R_q	roughness parameter (m)
769	V	velocity of blade (m s^{-1})
770	t	time (s)
771	x	distance travelled by blade (m)
772	t_c	transition point in decay behaviour (s)
773	t_{soak}	soaking time (s)

774

775 **Greek**

776	γ^{LS}	surface energy between liquid and solid phases (J m^{-2})
777	δ	soil layer thickness (m)

778

779 **Acronyms**

780	AFM	atomic force microscopy
781	CIP	clean in place
782	CMS	complex model soil
783	CTAB	hexadecyltrimethylammonium bromide
784	FDG	fluid dynamic gauging
785	LAS	linear alkyl sulfonate
786	MM3	millimanipulation mk 3
787	MM3-Flow	millimanipulation mk 3 with circulation system
788	SDBS	sodium dodecyl benzene sulfonate
789	SS	stainless steel
790	TX-100	t-octylphenoxyethoxyethanol

791

792 **Figure Captions**

793 Figure 1. Photographs of $\delta = 300 \mu\text{m}$ CMS layer on $50 \times 50 \text{ mm}$ 316 stainless steel
794 plate (a) before drying, and (b) after baking for 7 min at 204°C ; (c) Binary
795 image of (b) for calculating area of cracked soil; (d) image (b) with gridlines
796 used for calculating crack distribution.

797

798 Figure 2: Side view of the millimanipulation device with flow chamber fitted. Labels:
799 A, Perspex viewing wall; B, blade; C, force transducer; D, counterweight; E,
800 sample mounting station; I, solution inlet; O, solution outlet. Dashed arrow
801 indicates direction of sample motion.

802 Figure 3: Conductivity of solution leaving test chamber before and after addition of
803 NaOH solution to the reservoir at $t = 10 \text{ min}$. Data from three repeats. The
804 grey area indicates the section plotted in the inset. Solution flow rate 100 mL
805 min^{-1} .

806 Figure 4: Effect of contact with cleaning solution on residual soil on substrate. (a)
807 schematic of testing regions; (b) photograph of plate after testing with
808 (conditions for B: 5 minutes soaking in 1 wt% SDBS solution at room
809 temperature). All dimension in mm.

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822 subject to edge effects, repeated in subsequent plots. Dot-dashed lines mark the
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826 data in the range $50 < t < 350$ s. Vertical dashed lines mark initial and final
827 regions subject to edge effects.

828 Figure 10: Effect of pH on removal profiles at 50 °C. (a) pH 9, (b) pH 12: pH 7 data
829 given in Figure 8(b). Vertical dashed lines mark region A and D (edge effects).
830 Dot-dashed lines marks B/C transition observed at pH 7 at 220 s. Photographs
831 show substrate after testing.

832 Figure 11: Effect of surfactant on removal force at 20 °C. Soil is contacted with pH 9
833 solution at $t = 0$. Lines show linear regression to data in the range $50 < t < 350$
834 s. Vertical dashed lines mark initial and final regions subject to edge effects.
835 Photograph shows cleared region after testing with CTAB solution.

836 Figure 12: Effect of 1 wt% surfactant on removal profiles at pH 9 and 50°C. (a) CTAB,
837 (b) TX-100, (c) SDBS solution. Grey symbols show profile obtained without
838 surfactant (Figure 10(a)). Vertical dashed lines mark initial and final regions
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842

843 **Supplementary Figure Captions**

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845 plane AA'; (c) photograph. M indicates micrometers used to set the substrate-
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855 0.1 s⁻¹ the gradient is close to -1, associated with yield stress behaviour.

856

857 Figure S4: Effect of pH on removal profiles at 50 °C. Blue pH 6 D ~ 230, Grey pH 8 D
858 ~ 220. Vertical dashed lines mark region A and D (edge effects). Dot-dashed
859 line marks B/C transition, observed at 200 s for both pH 6 and 8. Image shows
860 an example of the substrate after testing. Note: F_w in section B is lower than that
861 measured at pH 7 for a different CMS batch (Figure 8(b)).

862

863 **Tables**

864 Table 1: Model soil composition

Component	mass fraction wet basis	nature	Supplier/source
fat	0.18	mixture of saturated and unsaturated fats	margarine blend 'I can't believe it's not butter™', whole milk
protein	0.057	milk protein	whole milk, Kraft cheese powder pasta (cooked)
carbohydrate	0.240	durum wheat starch	pasta (cooked)
salt	0.003	NaCl, dissolved	Kraft cheese powder
water	0.52	deionised water	pasta (cooked), whole milk

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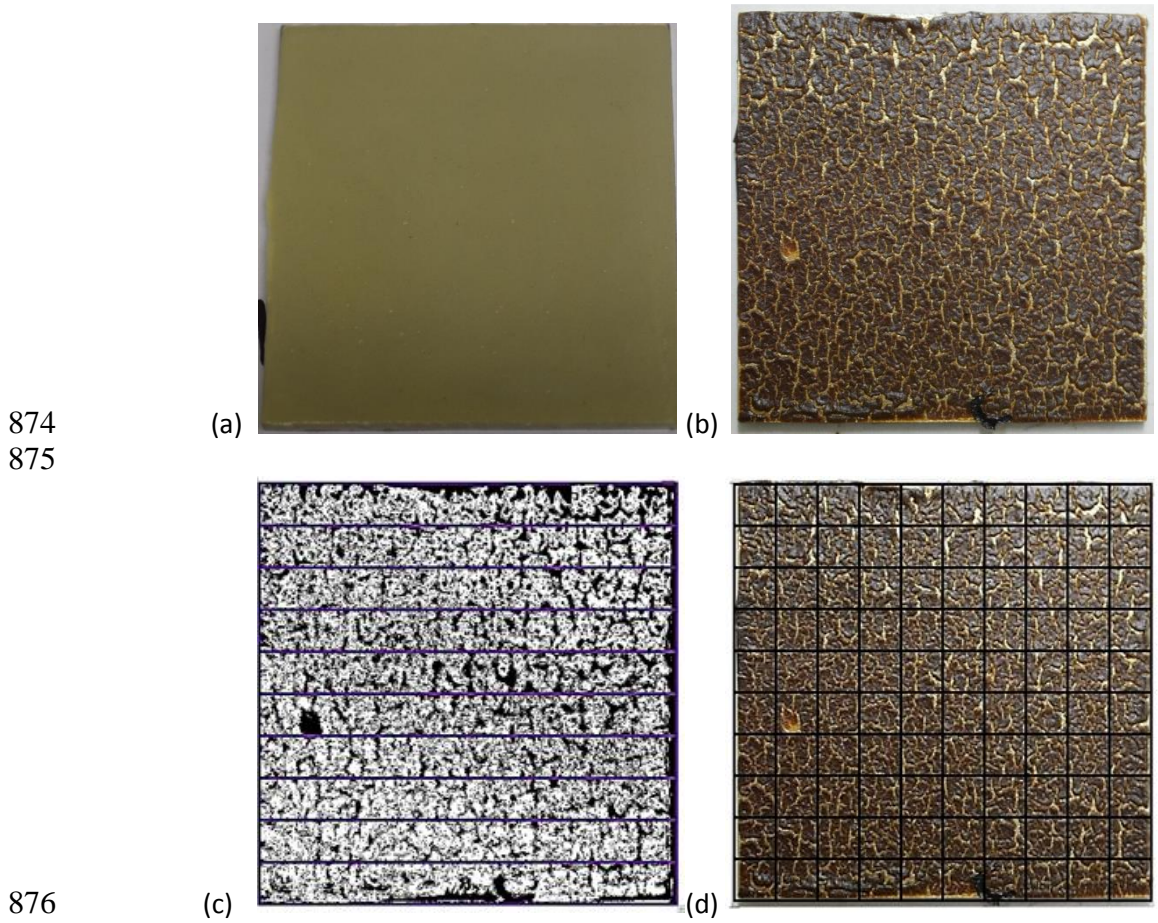
868 Table 2: Summary of rate of change of adhesion forces over 500 s testing. Values in
 869 parentheses are the uncertainty in the parameters, based on one standard
 870 deviation.

pH	surfactant (1 wt%)	t_c		linear decay rate		D	
		/s		$/\text{N m}^{-1}\text{s}^{-1}$		/s	
		20°C	50°C	20°C	50°C	20°C	50°C
7	-	-	220	0.06±0.007	0.51±0.01	-	125±3
9	-	-	220	0.15±0.02	0.26±0.01	-	-
12	-	-	300	0.11±0.01	0.26±0.01	-	-
9	SDBS	-	200	0.14±0.01	0.41±0.01	-	120±3
9	CTAB	40	40	0.42±0.01	-	213±4	238±5
9	TX-100	-	80	0.15±0.01	-	-	139±3

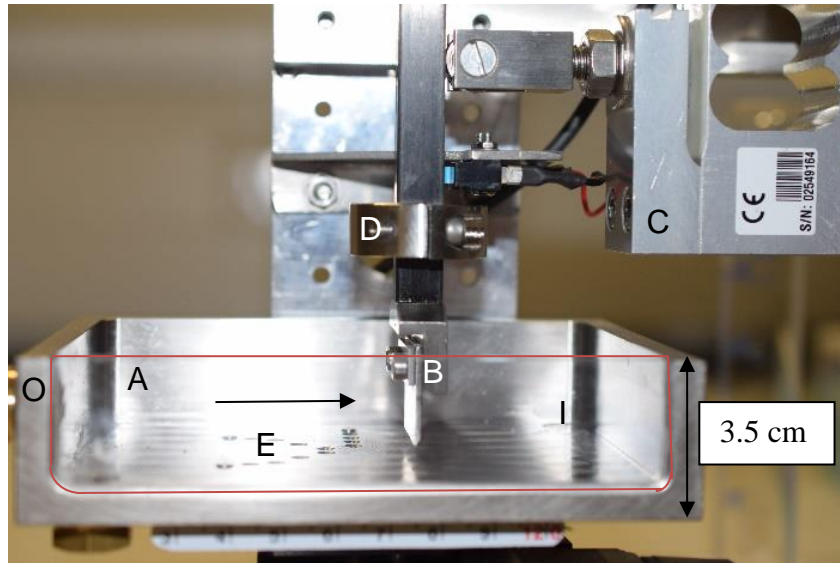
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872

873 **Figures**



879 Figure 1. Photographs of $\delta = 300 \mu\text{m}$ CMS layer on $50 \times 50 \text{ mm}$ 316 stainless steel
880 plate (a) before drying, and (b) after baking for 7 min at 204°C ; (c) Binary
881 image of (b) for calculating area of cracked soil; (d) image (b) with gridlines
882 used for calculating crack distribution.
883

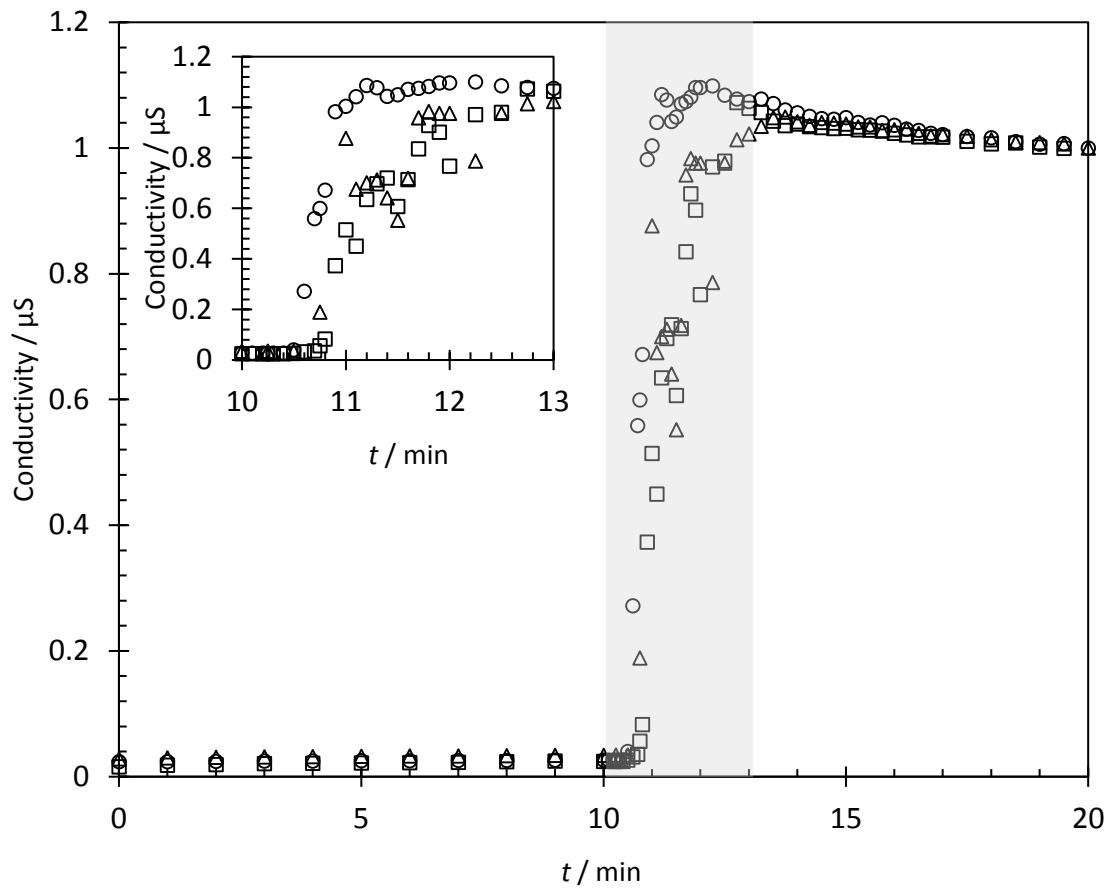


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886 Figure 2: Side view of the millimanipulation device with flow chamber fitted. Labels:
887 A, Perspex viewing wall outlined in red; B, blade; C, force transducer; D,
888 counterweight; E, sample mounting station; I, solution inlet; O, solution outlet.
889 Dashed arrow indicates direction of sample motion.

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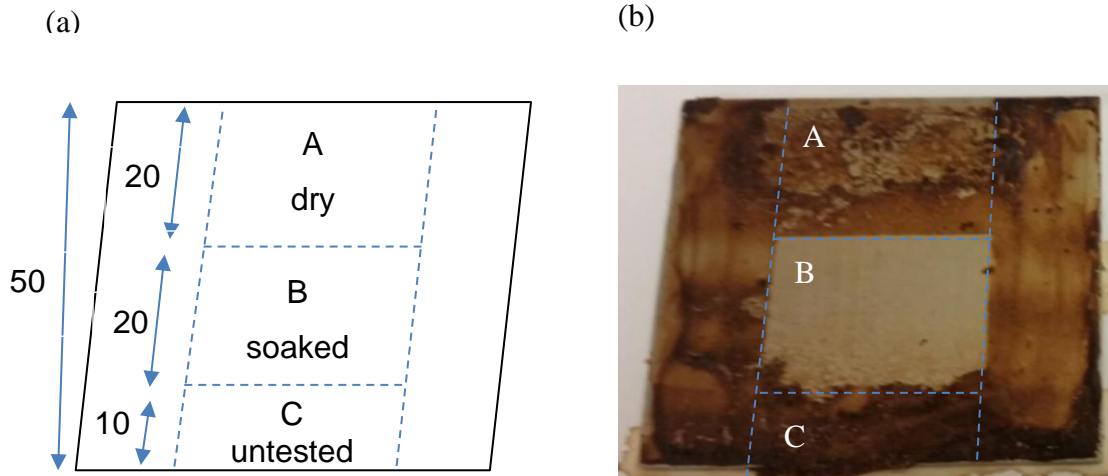


891

892 Figure 3: Conductivity of solution leaving test chamber before and after addition of
 893 NaOH solution to the reservoir at $t = 10$ min. Data from three repeats. The
 894 grey area indicates the section plotted in the inset. Solution flow rate 100 mL
 895 min^{-1} .

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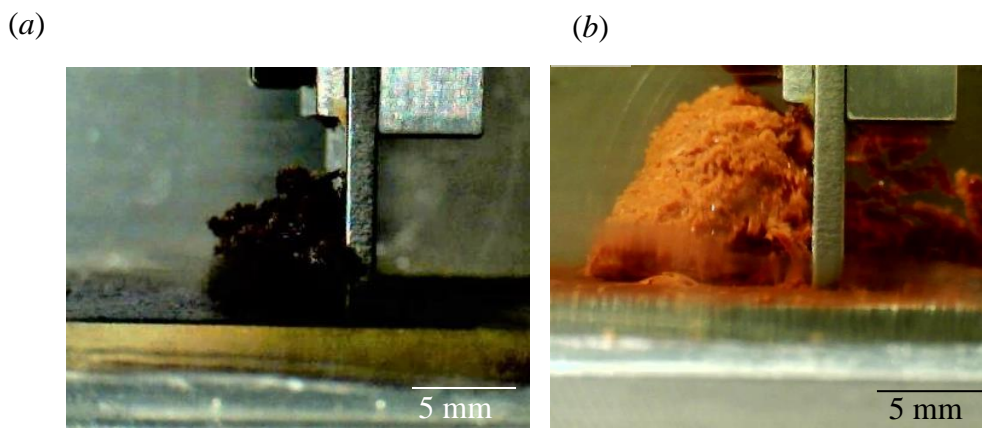
898

899

900 Figure 4: Effect of contact with cleaning solution on residual soil on substrate. (a)
 901 schematic of testing regions; (b) photograph of plate after testing with
 902 (conditions for B: 5 minutes soaking in 1 wt% SDBS solution at room
 903 temperature). All dimension in mm. Blade clearance: 50 μm .

904

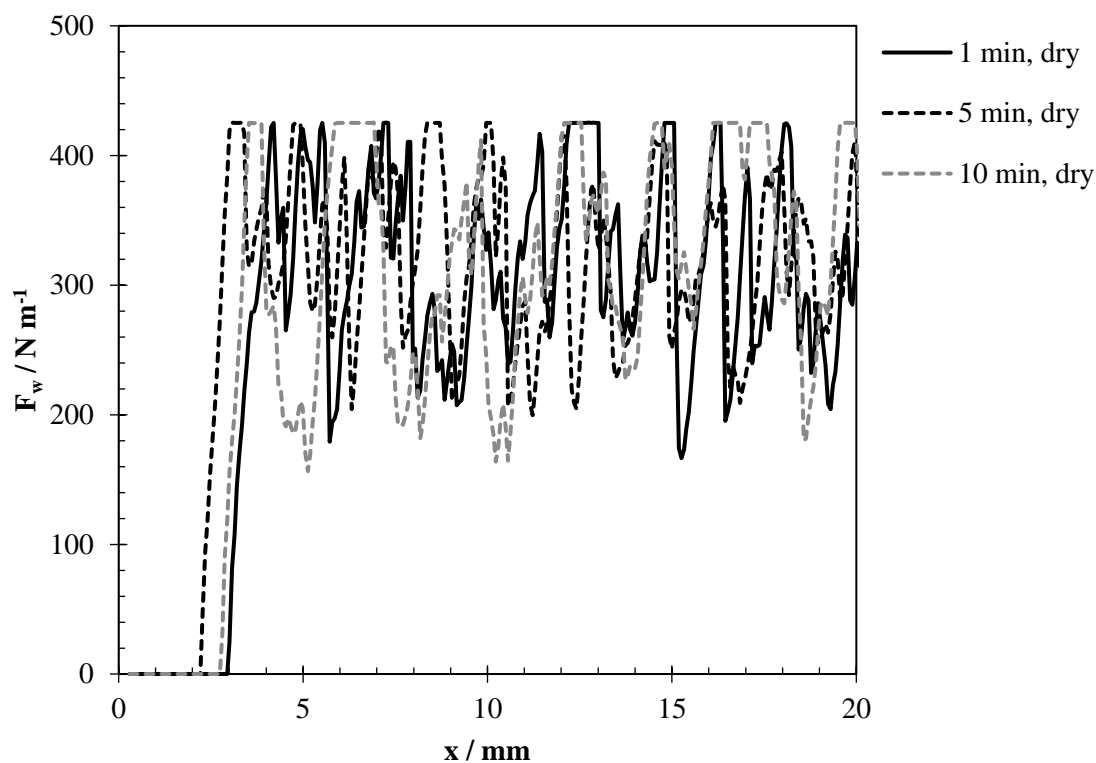
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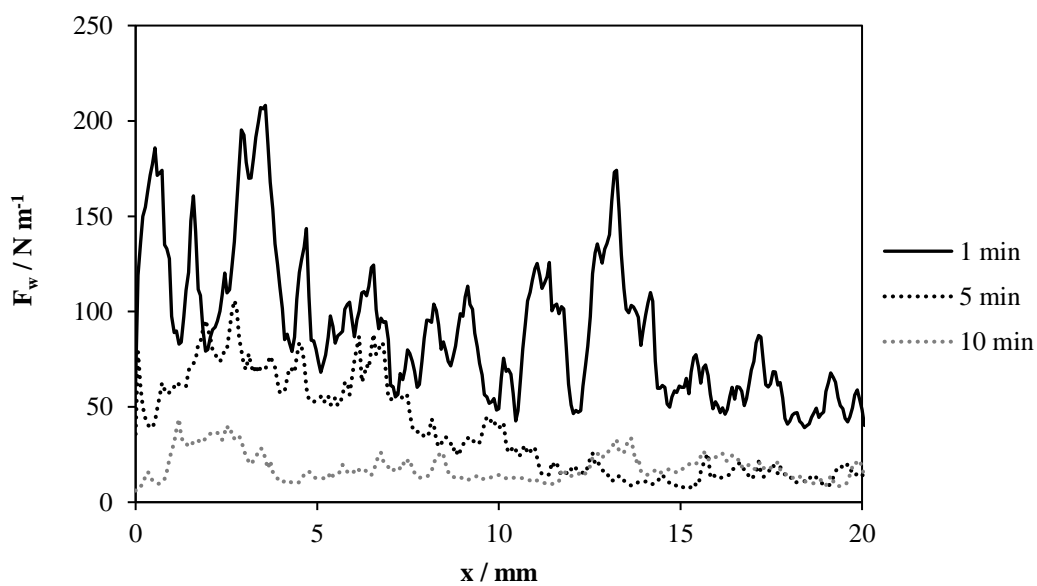
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910

911 (a)

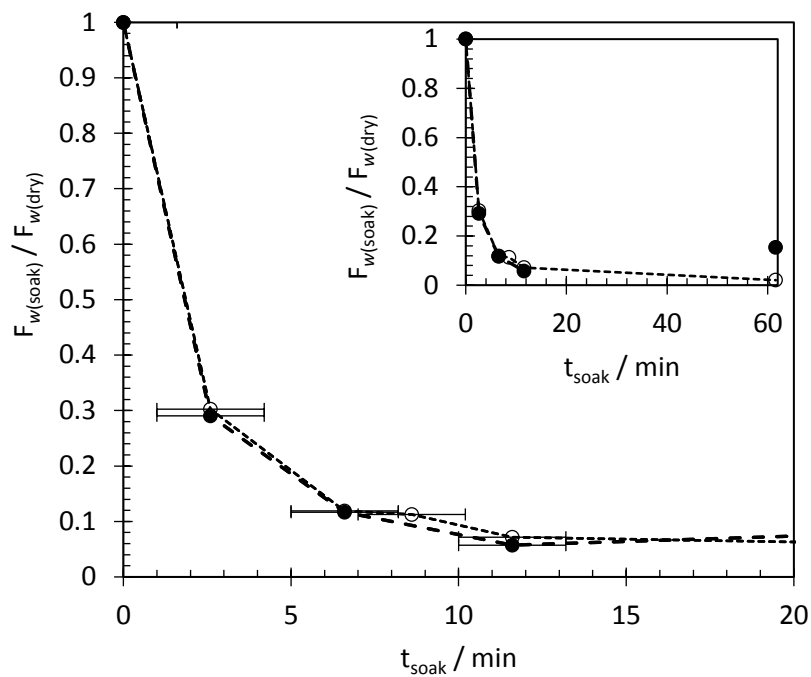


912 (b)



913

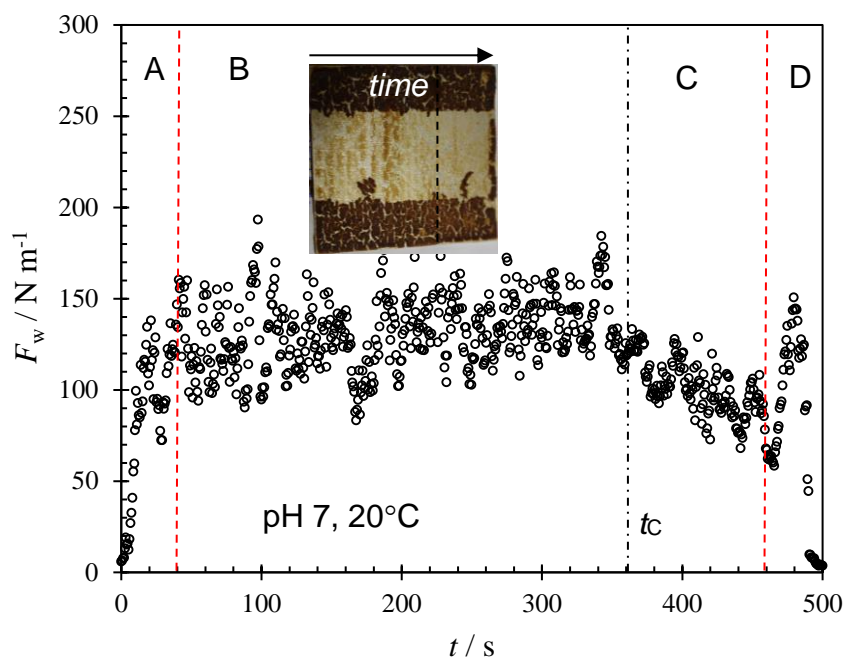
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918

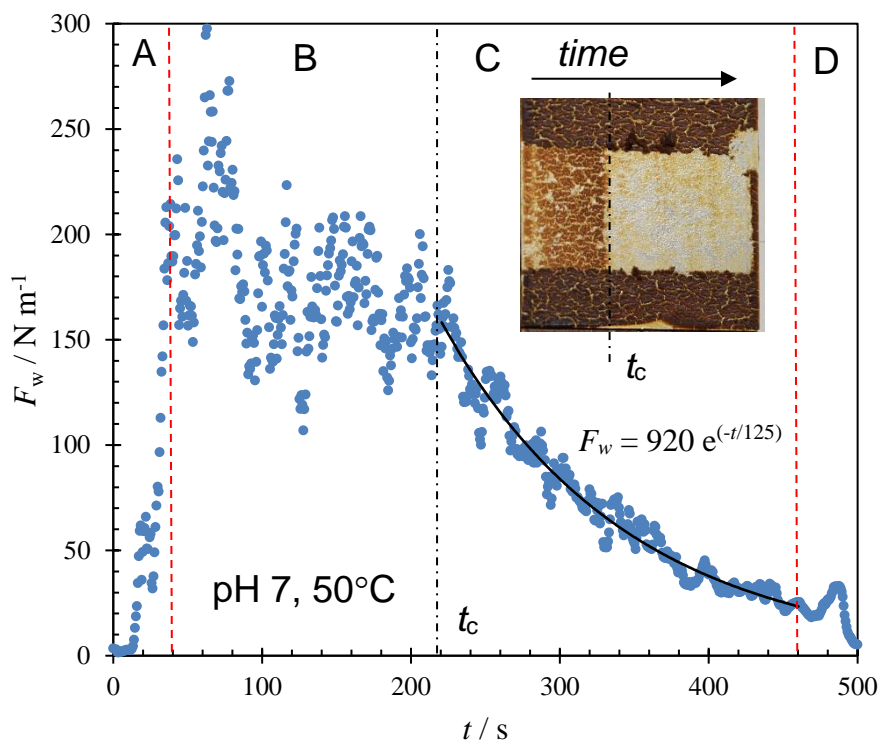
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 920 without 1 wt.% SDBS (open circles). Insert: full data containing 60 min data
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922 (a)



923

924 (b)



925

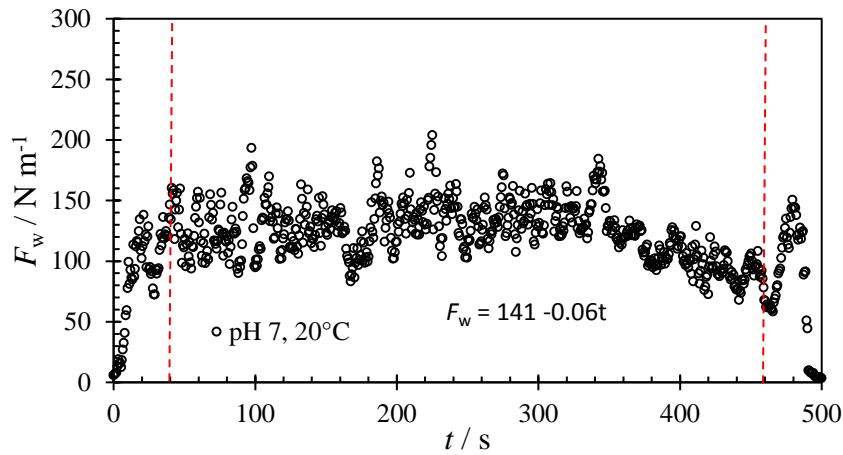
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927 at $t=0$ at (a) 20°C; (b) 50°C. Dashed vertical lines mark initial and final regions

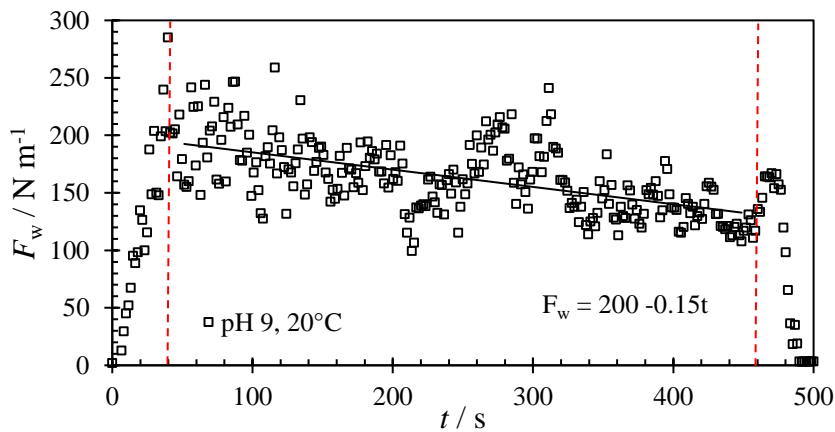
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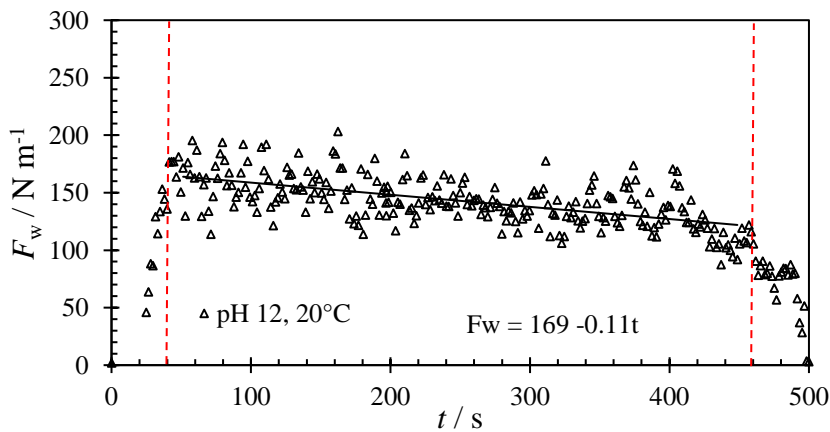
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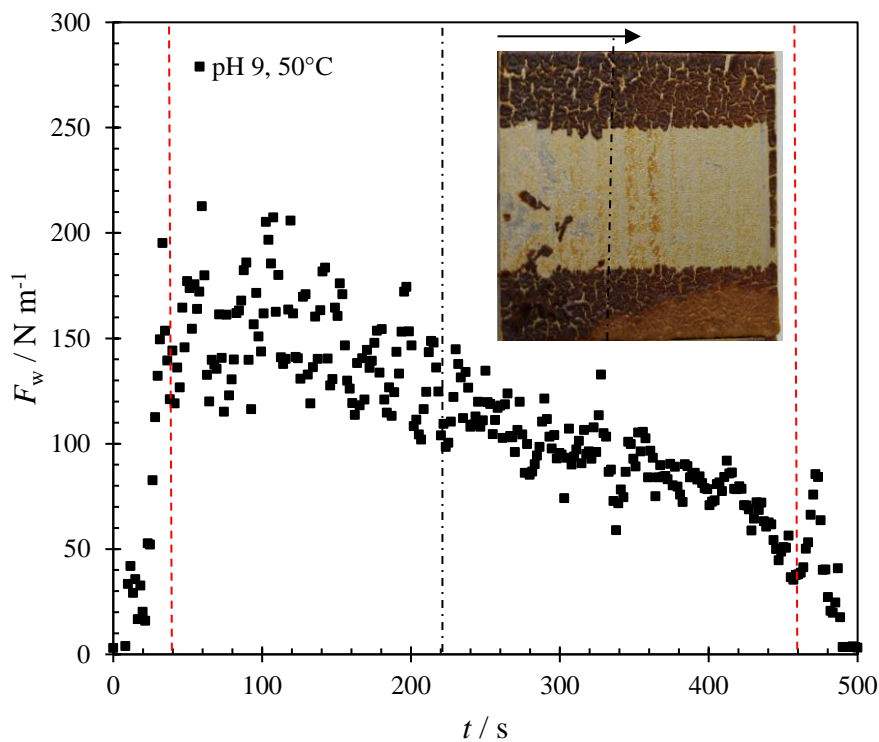


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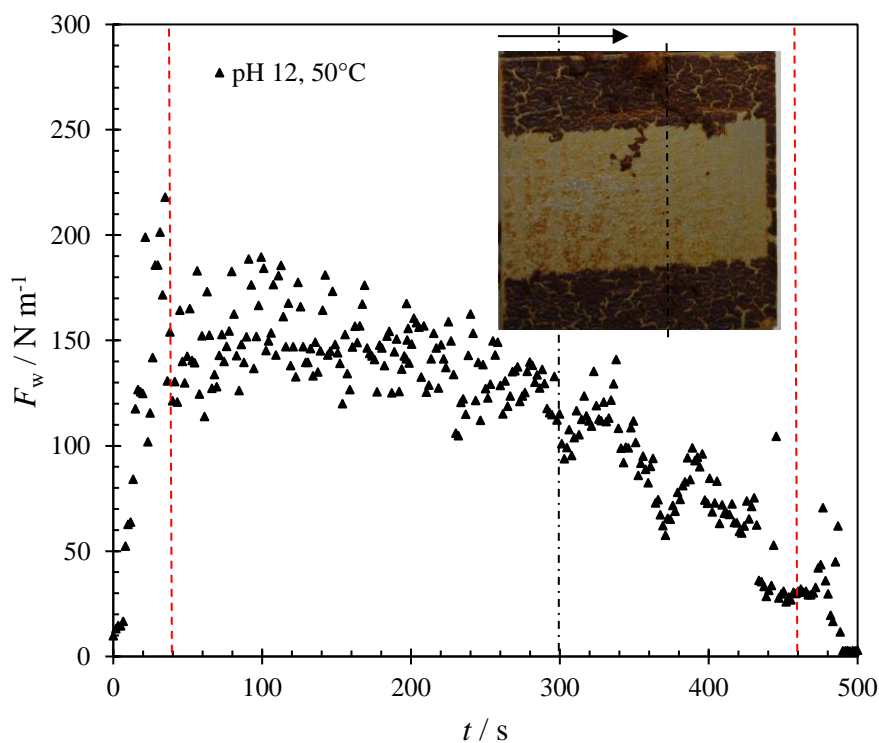
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937

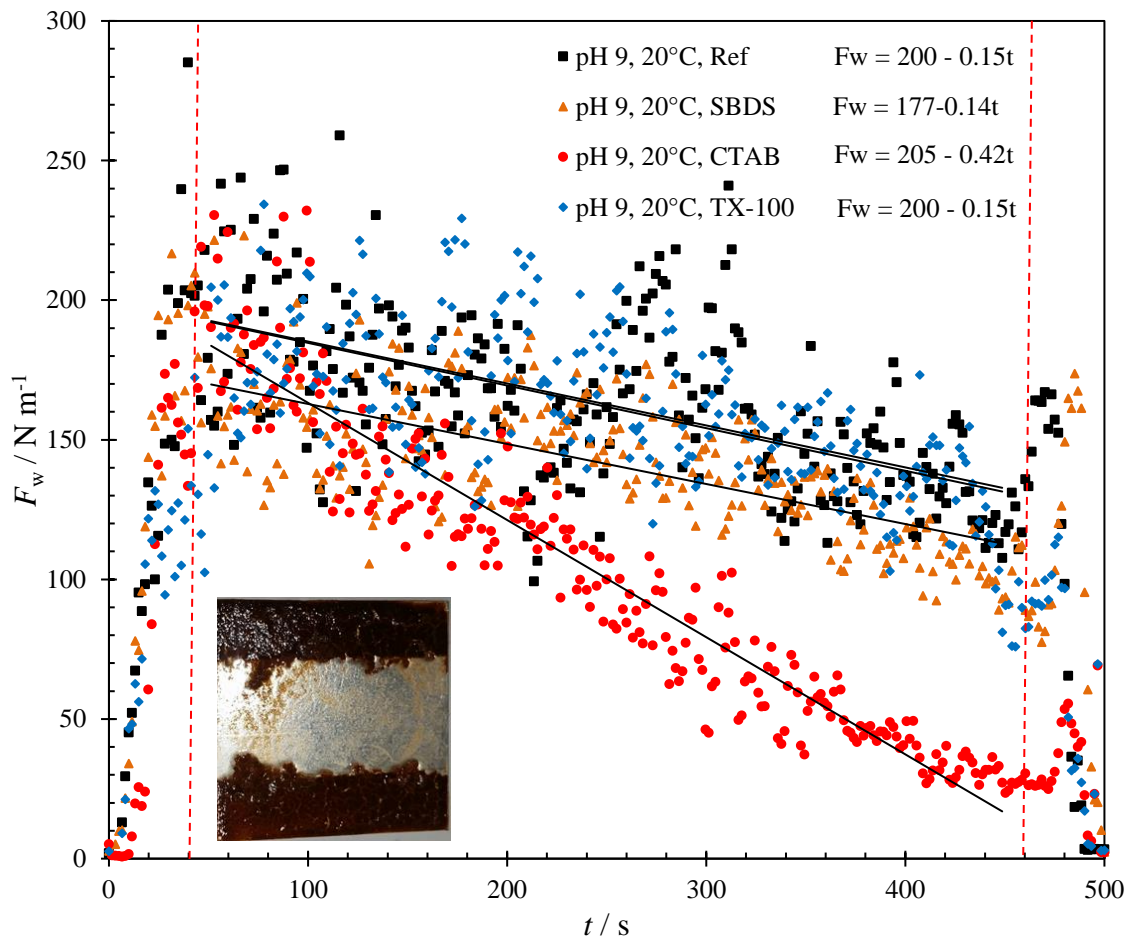
938 (a)



939
940 (b)



941
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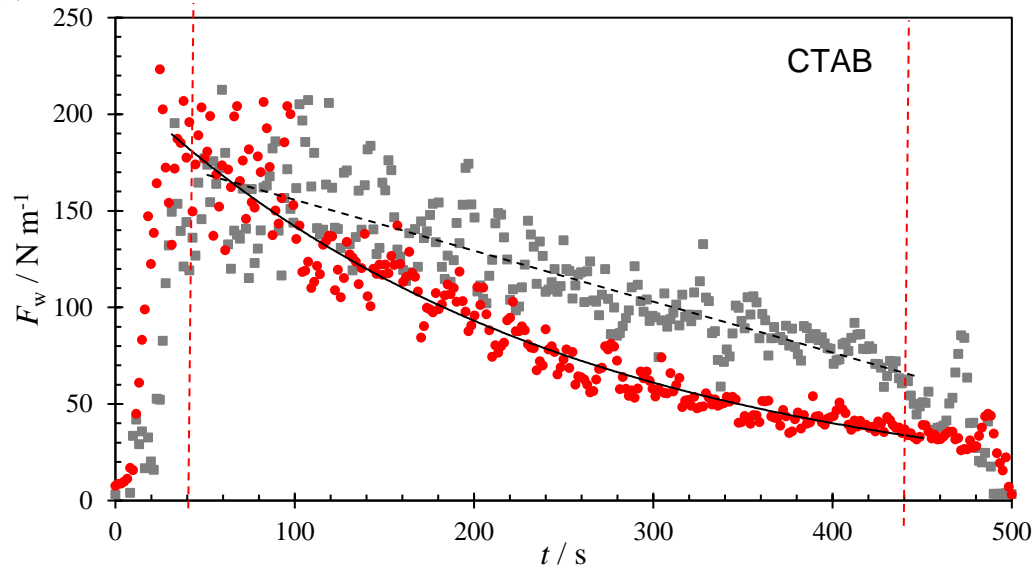
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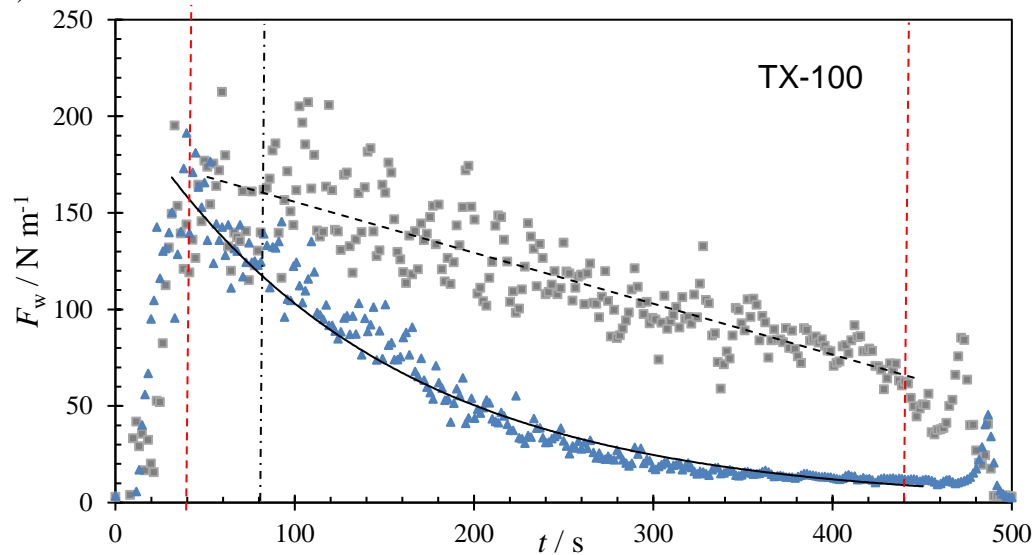
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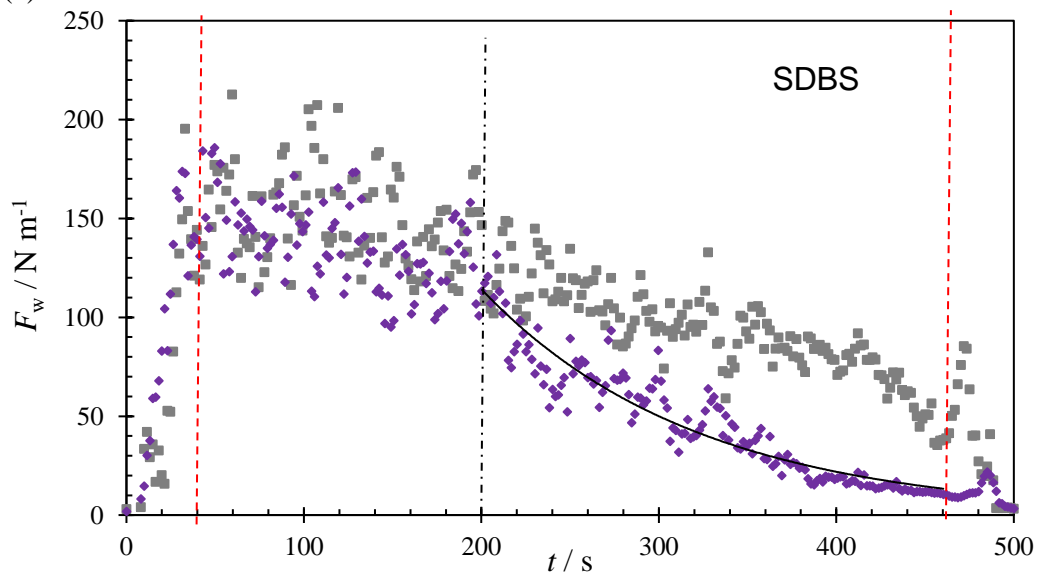
(b)



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(c)



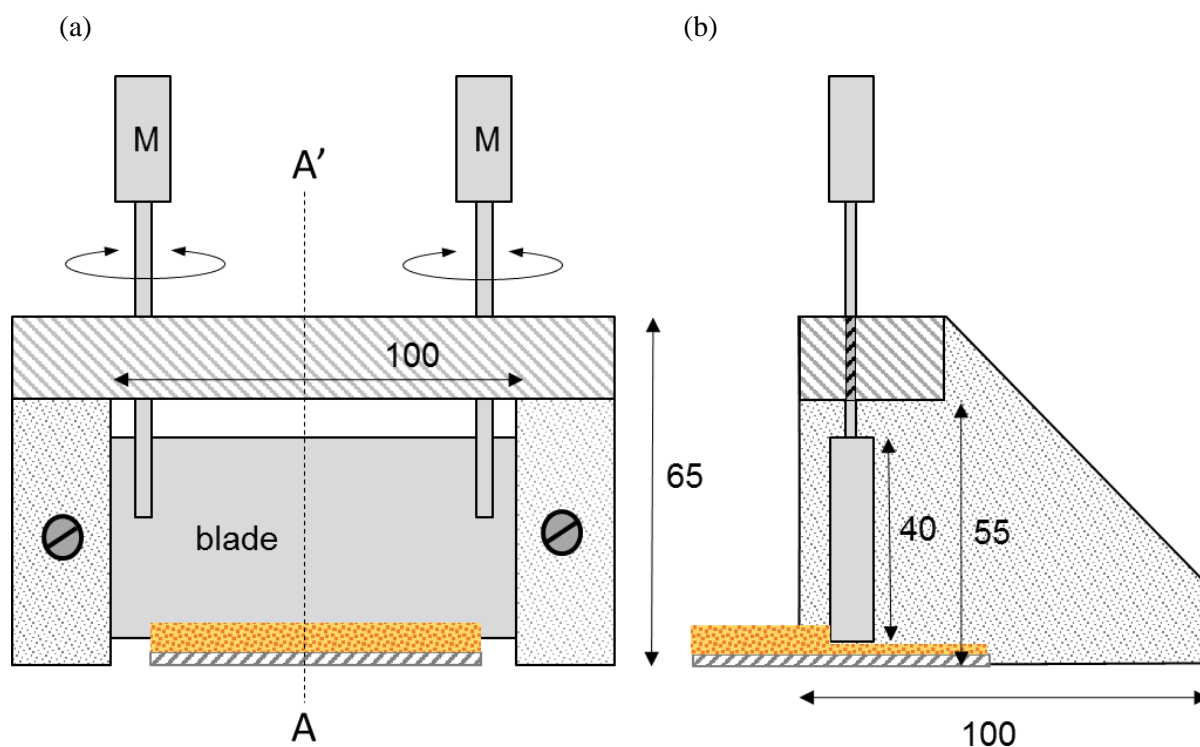
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964

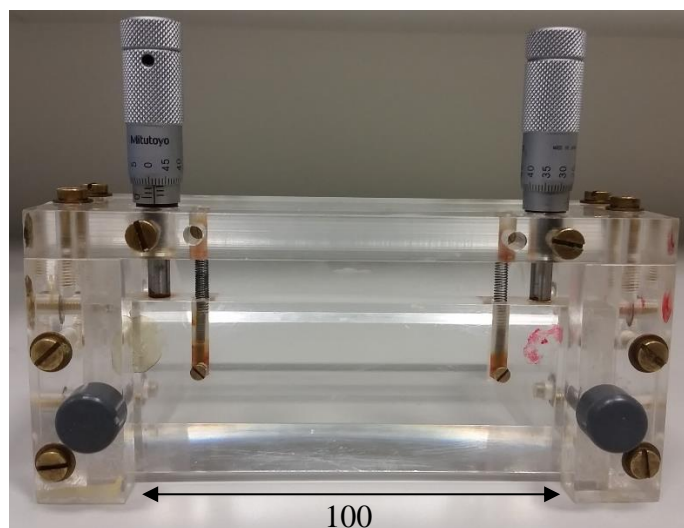
965 **Supplementary Figures**

966



967

968 (c)

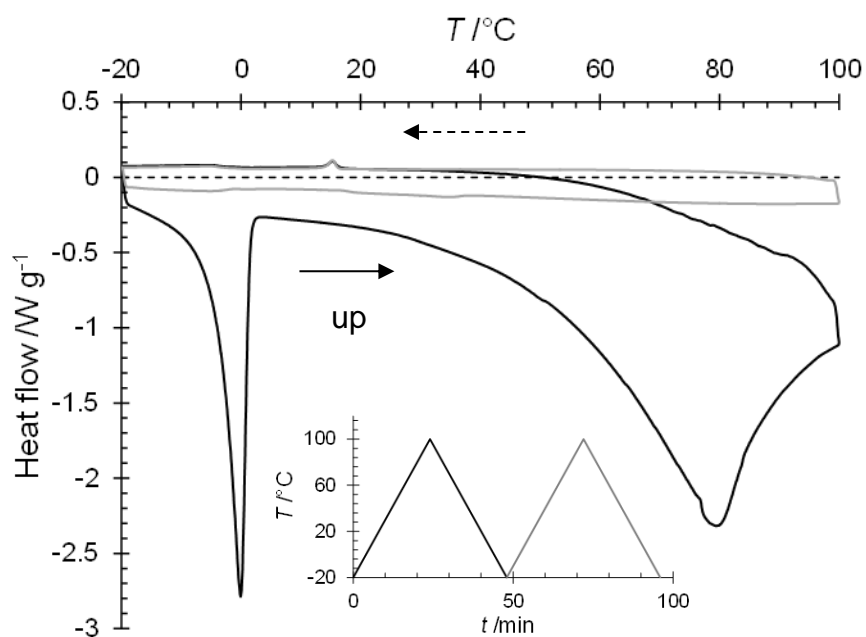


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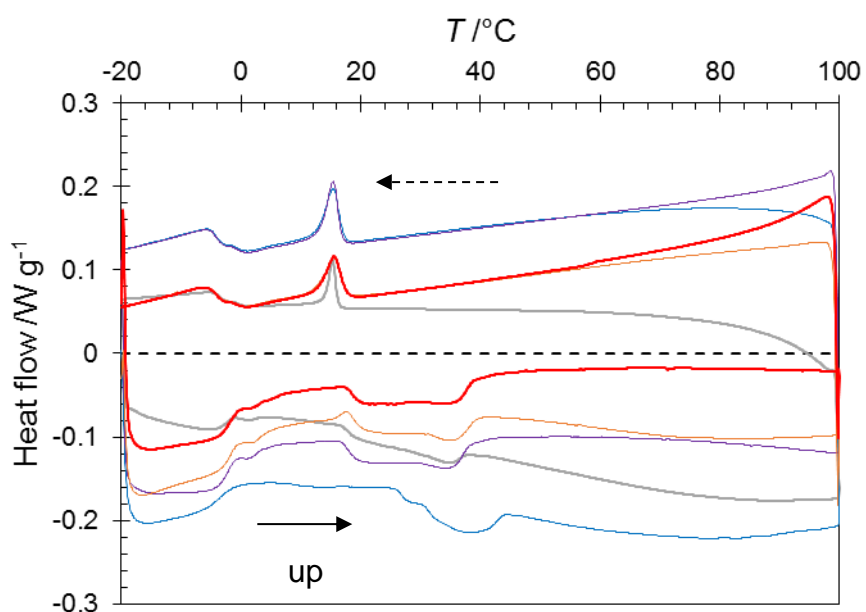
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973

974 (a)

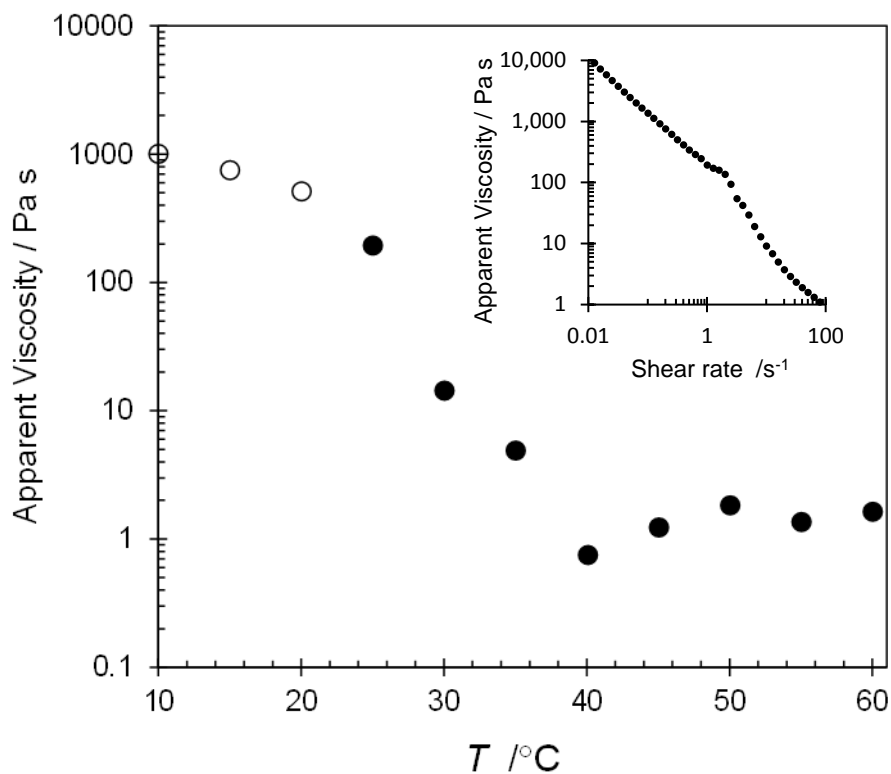


975
976 (b)



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978

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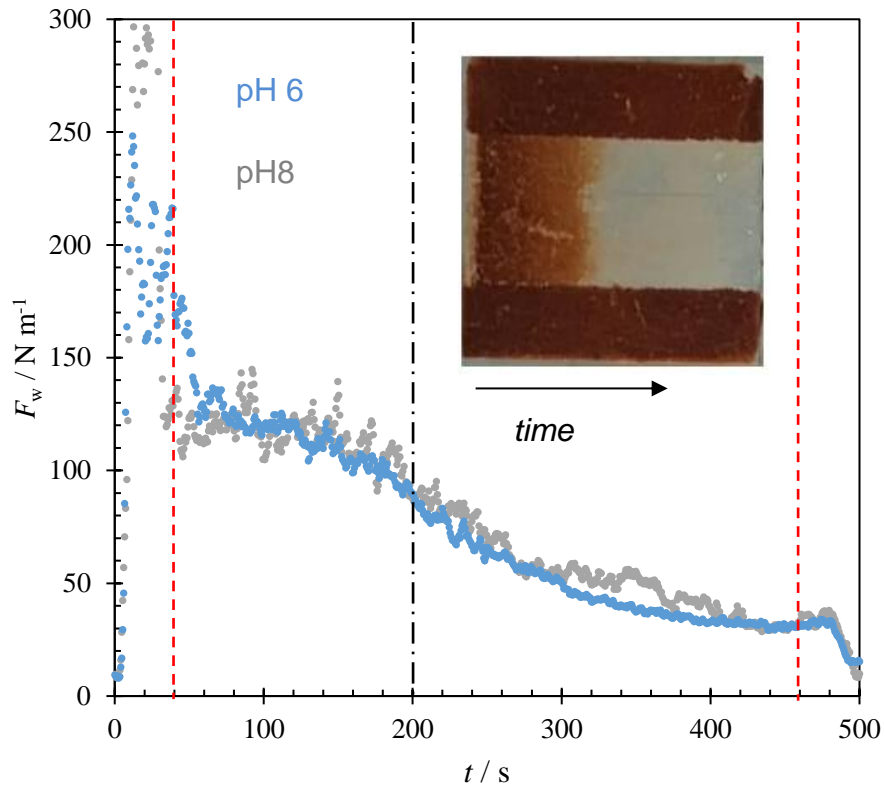
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