A FOULING MICRO-SYSTEM FOR INVESTIGATING FLUOROPOLYMER ANTIFOULING COATINGS IN BOVINE MILK PASTEURISATION

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ABSTRACT

Fouling of pasteurisation units processing raw milk reduces heat transfer and production capacity and gives rise to frequent heat exchanger cleaning. The associated extra operating costs and environment impact are substantial. Although a range of antifouling coatings has been proposed by researchers and industry, the problem still persists in practice. Testing antifouling coatings can require significant resources. A further consideration in studying pasteurisation fouling is that raw milk contains microbially active species so it would be advantageous to be able to screen coatings to identify candidates for plant-scale testing. A micro-scale heat exchanger system was constructed to study fouling under surface temperatures and wall shear stress conditions representative of sections on a high temperature short time (HTST) pasteuriser. The apparatus features a 650 × 2000 µm flow channel which enables fouling studies to be carried out with batches of approximately 2 litres of raw milk. The pressure drop across the unit is monitored over time and the deposit can be inspected in-situ with confocal laser scanning microscopy. Tests were conducted on stainless steel and fluoropolymer coated stainless steel heat transfer surfaces. Compared to steel, a smooth fluorinated ethylene propylene coating reduced deposit attachment by ~30% and pressure drop increase by ~50%. The effects of the surface free energy, roughness and coating material on the amount and type of deposit formed are discussed.

INTRODUCTION

Milk fouling, the accumulation of deposits from milk products on heat transfer surfaces, accounts for a major fraction of operating costs in dairy processing. Fouling increases resistance to heat transfer, pressure losses, cleaning costs and compromises product quality and safety (Sadeghinezhad et al., 2013).

The two main constituents found in milk fouling deposits – and key species involved in deposition – are calcium phosphate and whey proteins (Bansal and Chen, 2006; Sadeghinezhad et al., 2013). Tolkach and Kulozik (2007) described the aggregation and polymerisation pathway of β-lactoglobulin (BLG), a heat sensitive globular whey protein, as involving the steps shown in Fig. 1: at physiological conditions BLG is present as a dimer (labelled N₂), dissociating reversibly at temperatures above around 40 °C into two native monomers (2N). At temperatures from 40 to 55 °C some side chains undergo minor reversible conformational changes, improving accessibility of its free thiol group. In this, so-called R-state (N₁), BLG can polymerise, albeit at very low rates. Above 60 °C BLG partially unfolds and exposes the free thiol group. In this stage, called the molten globule state (U₂M), intramolecular disulphide exchanges become possible, rendering the transition irreversible. Exposed non-polar patches facilitate the association of BLG to and from aggregates (U₃), simultaneously taking part in thiol exchange reactions to form a polymer (U₄). Above 130 °C native BLG unfolds completely and loses its secondary structure. Calcium ions mediate the aggregation by screening electrostatic repulsion (Simons et al., 2002). The presence of a solid surface may lead to adsorption and deposition at all of these stages, most notably via hydrophilic attraction and covalent bonds. The ability of surfaces to participate in hydrophilic attraction is determined by their surface energy (van Oss, 2003).

Concomitantly, the solubility of calcium phosphate decreases with temperature (Bansal and Chen, 2006). This leads to nucleation and growth of calcium phosphate crystals on the heat transfer surface and in the bulk liquid. Hagsten et al. (2016) showed that particles formed in the bulk can also adhere to the surface, which creates a complex composite matrix on many length-scales. They used confocal laser scanning microscopy and fluorescent dyes exhibiting an increase in fluorescence upon binding to investigate the structure and composition of deposits formed in high temperature (milk stone) fouling.

Although the mechanisms in dairy fouling are qualitatively understood (Sadeghinezhad et al., 2013), few effective strategies have been identified to reduce deposit formation or its consequences in practice. One approach is the use of antifouling coatings to minimise adhesion or mediate the build-up of deposit which is easy to clean. Some studies demonstrate the effect of the surface on deposit composition (Boxler et al., 2014) but to the authors’ knowledge few studies have considered the spatial distribution of the species on non-metallic surfaces.
The sequence of events in dairy fouling has been debated at length. With stainless steel, some studies have reported a high concentration of minerals close to the heat transfer surface at 100 and 140 °C (Foster and Green, 1990; Foster et al., 1989), whereas others stated that they found a dense sub-layer and could not measure a difference in composition (Hagsten et al., 2016). The experimental timescales in these studies differed, which may have had an influence on the hierarchical structures observed.

This paper reports the development and use of a scaled down heat exchanger to investigate milk fouling on different surfaces. Visser and Jeurnink (1997) stated that fouling is controlled by reactions taking place in the bulk above 72 °C and the subsequent deposition of any particles thus formed. In the micro-heat exchanger the bulk temperature does not exceed this threshold and these reactions only occur at the heat transfer surface. The system is designed to use raw milk, to avoid Mérian and Goddard (2012)'s criticism of antifouling testing using simple formulations which do not represent the complexity of real foodstuffs.

MATERIALS AND METHODS

FOULING MICRO-SYSTEM

The fouling micro-system is based around the fouling cell shown in Fig. 2. The cell has three main functions: (i) guiding the flow of the process fluids into the cell, past the test surface and out, (ii) heating the square test plate (dimension 50×50×2 mm) to the desired surface temperature and (iii) allowing microscope imaging.

The cell is constructed as a composite sandwich with cross section depicted in Fig. 2 (b). The channel body (labelled 1 on the Figure) is made of 3D printed polyamide PA2200 (3Dprintuk Ltd.) and holds a 180 μm thick borosilicate glass slip (2) on a stainless steel support shim. The walls of the channel are made of cast silicone rubber which also acts as a seal against the sample surface (3). The test plate is heated by a positive temperature coefficient heater (4) and the temperature of the heater, \( T_h \), is measured by a thermistor. The sample and heater are embedded in silicone rubber insulation (5). The cell is clamped with eight screws (6) via a compression plate (7) fabricated from acrylonitrile butadiene styrene on a MakerBot 2x 3D printer. The channel created between the glass slip and test surface is rectangular with dimensions \( a \times b = 2 \times 0.65 \) mm², see Fig. 2 (c). This was confirmed at the cell operating temperatures by confocal chromatic thickness measurement (Micro-Epsilon GmbH & Co. KG, IFS2405-3). The heat transfer area, \( A \), is \( \alpha x L = 80 \) mm². When being imaged the cell is located on the optical \( xyz \)-stage of an inverted confocal laser scanning microscope (CLSM), with the base plate machined to incorporate the lens (8).

Fig. 3 shows how the fouling cell is integrated into the experimental system. Batches of deionised water, raw milk and 1M sodium hydroxide are held at 56 °C in separate containers in a heated water bath (9). The selected liquid is drawn successively by individual proportional-integral controlled peristaltic pumps (10) with a flow rate of 12.1 ±0.67 g/min (±standard deviation, otherwise indicated) and fed through a spiral copper tube in a second bath held at 63 °C (11). BLG aggregation starts at this temperature. The liquid is then pumped through the fouling cell (12).

![Fig. 2 Fouling microcell assembly. Labels are explained in the text. (a) Side view, inlet facing front. (b) Cross section through plane AA showing channel, sample and heater. (c) Magnification of (b) showing sample and channel geometry. The width of the channel is 2 mm. Dash-dot lines indicate planes of symmetry.](image)

![Fig. 3 Micro fouling system schematic. Labels explained in text.](image)
board programmed in C/C++. Higher level functions, such as set-point generation, data visualisation and storage, are programmed in a Python 2 module executed on a standard PC. The microcontroller and PC communicate bidirectionally via a USB connection and data are stored every five seconds.

The electrical power supplied to the heater, $Q_e$, is transferred to the fluid, $Q$, or the environment, $Q_{env}$:

$$Q_e = Q + Q_{env}$$  \hspace{1cm} (1)

Experiments are performed under constant heat-flux conditions, i.e. fixed power rating. The desired mean sample surface temperature, $T_{s,m}$, is set and the steady state power input, $Q_e$, is calculated accordingly. This mode of operation has two advantages: the surface temperature is independent of (i) the heat transfer resistance of the sample, and (ii) the fouling resistance, if the fouling layer is thin and does not affect the film heat transfer coefficient. The heat loss to the environment, $Q_{env}$, was characterised as a function of heater temperature, $T_h$, and the temperature of the environment, $T_{env}$, in separate tests with mass flow rate, $\dot{m} = 0$. The electrical power requirement is calculated from

$$Q_e = \left( T_{s,m} - \frac{T_{m} + T_{in}}{2} \right) A h_{f,m} + Q_{env} (T_h, T_{env})$$  \hspace{1cm} (2)

where $h_{f,m}$ denotes the mean film heat transfer coefficient. The thermophysical properties of raw milk are approximated as those of water (VDI, 2010) apart from the viscosity, which was taken from Fernández-Martín (1975) for milk with 10 wt% total solids content. The Reynolds number in the test channel, $Re$, was 213±12, so laminar flow is expected. The average Nusselt number was estimated from numerical solutions for thermally developing laminar flow in rectangular channels heated from four sides reported by Wibulsvas (1966) for the following conditions:

(i) The channel is a simple rectangular duct. For simplicity, this is approximated by assuming a uniform channel height of 0.65 mm.

(ii) The hydraulic boundary layer develops more quickly than the thermal boundary layer. The Prandtl number, $Pr$, at the inlet in this case is 4.8 and indicates faster momentum diffusion than thermal diffusion.

(iii) The wall heat flux along, and temperatures perpendicular to, the main channel axis are uniform. This approximates the configuration in the fouling cell.

Table 1 summarises the Nusselt numbers for a channel of aspect ratio around 1/3.

<table>
<thead>
<tr>
<th>$\chi^{*}$</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>80</th>
<th>120</th>
<th>160</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Nu_{m}$</td>
<td>4.77</td>
<td>6.06</td>
<td>7.09</td>
<td>8.48</td>
<td>9.52</td>
<td>10.31</td>
<td>10.97</td>
</tr>
<tr>
<td>$Nu_{a}$</td>
<td>4.77</td>
<td>5.00</td>
<td>5.39</td>
<td>6.21</td>
<td>6.92</td>
<td>7.50</td>
<td>8.02</td>
</tr>
</tbody>
</table>

The dimensionless coordinate, $x^*$, is defined as $x/D_h Pe$, where $x$ is the axial distance along the channel (see Fig. 2(c)), $D_h$ is the hydraulic diameter, and $Pe = Re Pr$ is the Péclet number. The mean and local film heat transfer coefficient can be obtained from $h_f = Nu_{k}k_{m}$, where $k$ is the thermal conductivity of the milk. The local surface temperature, $T_s$, is found from the overall enthalpy balance

$$T_s = \frac{\dot{m}c(T_{out} - T_{in}) + T}{Ah_f}$$  \hspace{1cm} (3)

Here $c_p$ is the (almost temperature insensitive) specific heat capacity and $T$ is the bulk temperature, which increases linearly along the channel:

$$T = (T_{out} - T_{in})x/L + T_{in}$$  \hspace{1cm} (4)

Fig. 4 shows the initial temperature distribution in the clean fouling cell. It can be seen that the temperature in the thermal boundary layer favours BLG being in the molten globule state. Protein deposition accompanied by an increase in $\Delta P$ are expected to occur. The change in pressure drop can be related to the deposit thickness, $\delta$, via the Hagen–Poiseuille equation (Sutera and Skalak, 1993):

$$\Delta P = \frac{128}{\pi} L\mu \left( \frac{a + b - \delta}{2a(b - \delta)} \right)^4$$  \hspace{1cm} (5)

where $a$ and $b$ are the channel width and height, respectively. If the deposit is thin compared to the channel dimensions, this can be written as:

$$\Delta P \propto (b - \delta)^4$$  \hspace{1cm} (6)

This result assumes that the layer has uniform thickness. The pressure drop is significantly more sensitive to deposit build up than the overall heat transfer coefficient, which is proportional to the layer thickness of the deposit.

![Fig. 4 Estimated bulk and surface temperature distribution in the fouling cell for standard operating conditions. Error bars indicate standard deviations. The schematic on the right illustrates the temperature dependency of BLG structural changes in Fig.1.](image-url)
CONFOCAL LASER SCANNING MICROSCOPY

CLSM was used to study the distribution of calcium phosphate and protein within the fouling layer. Calcium green A1 (CG) and Texas red sulfonyl chloride (TR-SC) (Molecular Probes Inc.) show an increase in fluorescence on binding to calcium ions and amine groups, respectively. 50 μg of CG was dissolved in 40 μl dimethyl sulfoxide (99+ % (g/g), Alfa Aesar) under ultra-sonication and added to 10 ml deionised water. The final concentration of ~4 μM is similar to that used by Thomas et al. (2000) to observe calcium cell signalling. The solution was injected into the test cell and kept there for 25 min. 1 mg of TR-SC was dissolved in 10 ml deionised water just above the water freezing point to reduce the rate of dye hydrolysis (Lefevre et al., 1996). The 160 µM TR-SC solution was injected into the cell shortly after mixing and again held therein for 25 min. The cell was then rinsed with deionised water and placed on a Leica TCS SP5 CLSM. The CG and TR-SC fluorophores were excited by an argon laser at 514 nm and a helium-neon laser at 633 nm. Images of deposits on fluoropolymers were taken in situ with a 10× air lens and the pinhole set to 53 μm. The strong adhesion of deposits to stainless steel allowed them to be imaged ex-situ using a 40× oil immersion lens.

RAW MILK

Raw milk from Holstein-Friesian cattle was sourced from the University of Cambridge’s Park Farm and used on the day of experiment. The cows were fed a diet optimised for milk yield including maize and grass silage, malt residue, potatoes, rumen protected fats and other supplements. The calcium content of the milk was determined with inductively coupled mass spectroscopy to be 0.095 % (g/g). The unmodified milk was deaerated for 45 min in an ultrasonic bath at 20 KPa (absolute) and 56 °C, i.e. just below its boiling point. The pH of the raw milk as received at 6 °C was 6.7 ±0.24 and dropped to 6.3 ±0.06 after heating to 56 °C for degassing. During degassing the pH increased slightly. CLSM images of the milk indicated no visible effect of the procedure on the milk fat globules.

SURFACES TESTED

Properties of the surfaces investigated are summarised in Table 2. Four coatings were applied to square stainless steel plates (material: EN 1.4301 304, surface finish EN 10088-2 2R). Perfluoroalkoxy was applied as a powder (PFA-2) and as a water based-liquid (PFA-3). Fluorinated ethylene propylene (FEP) was applied as a water-based liquid (FEP-2). In contrast, sample PTFE-1 is an epoxy resin with dispersed polytetrafluoroethylene (PTFE) particles. Coating thickness was measured by micrometer, as the difference between the thickness of the coated plate and the plate after the coating had been scraped off. The thermal conductivity was calculated from the thickness and the difference in clean overall heat transfer coefficients, measured in the fouling cell, for coated and uncoated plates. The surface topology was mapped with a Zygo NewView 200 interferometer to deduce roughness parameters (ISO 25178) summarised in Table 2. Further information about the coatings is given in Magens et al. (2017).

<table>
<thead>
<tr>
<th>Surface</th>
<th>δcoat (μm)</th>
<th>kcoat (W/m K)</th>
<th>Sa (nm)</th>
<th>Sdr (nm)</th>
<th>Si (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>—</td>
<td>—</td>
<td>±3</td>
<td>±4</td>
<td></td>
</tr>
<tr>
<td>PFA-2</td>
<td>102 ±8.2</td>
<td>0.27 ±0.04</td>
<td>490 ±47*</td>
<td>±58*</td>
<td></td>
</tr>
<tr>
<td>PFA-3</td>
<td>71 ±3.5</td>
<td>0.27 ±0.04</td>
<td>560 ±67*</td>
<td>±80*</td>
<td></td>
</tr>
<tr>
<td>FEP-2</td>
<td>58 ±3.3</td>
<td>0.15 ±0.02</td>
<td>380 ±78*</td>
<td>±92*</td>
<td></td>
</tr>
<tr>
<td>PTFE-1</td>
<td>42 ±3.4</td>
<td>0.12 ±0.03</td>
<td>740 ±73*</td>
<td>±110*</td>
<td></td>
</tr>
</tbody>
</table>

*taken from Magens et al. (2017).

The dispersive, electron donor and electron acceptor surface energy components were determined by non-linear regression according to the van Oss (1987) method with high purity deionised water, formamide, ethylene glycol and dodecane. Equilibrium contact angles were measured 12 times and the results are given in Table 3. Surfaces can be either considered monopolar (van Oss et al., 1987), or non-polar. SS is the highest energy and most polar surface, followed by PTFE-1 which also displays significant polarity, presumably due to the epoxy matrix (c.f. Berghsien et al. (2004)). The other fluoropolymers are non-polar and have low Lifshitz-van der Waals interaction parameters.

EXPERIMENTAL PROTOCOL

Fig. 5 shows an example of the evolution of the monitored variables during a fouling test. Initially, de-aerated and deionised water was pumped through the cell until thermal steady state was reached for the desired mean surface temperature (marked t1 in Fig. 5). The flow rate was 12 g/min for all experiments. The liquid was then switched to de-aerated raw milk and the Figure shows a steady increase in ΔP as deposition occurred. The heater temperature would be expected to increase as the associated thermal resistance grew. In most experiments, however, the change in thermal resistance was not significant over the range of conditions and time-scales studied. At time t2 the fouling cell heater was turned off and cooled to 75 °C with deionised water. The flow then stopped and the cell was either studied with CLSM or disassembled to remove the test plate and dry the deposit before weighing.

Following an experiment the test plate and channel body (l) in Fig. 2(b) were cleaned in six steps: (i) washed with a commercial dishwashing detergent, (ii) rinsed with water, (iii) washed with 1M NaOH, (iv) rinsed with water, (v) washed with 0.5 M phosphoric acid and (vi) rinsed again. The rest of the system was cleaned by circulation of 1M NaOH followed by deionised water. Test plates were reused and the clean performance was monitored to determine whether irreversible changes occurred.
Table 3 Equilibrium contact angle, $\beta$, measured at 20°C, and surface energy components calculated from the van Oss theory (van Oss et al., 1987). Liquid parameters taken from van Oss et al. (1992). Angles are reported to one decimal place. ± indicates standard deviation.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Contact angle (°)</th>
<th>$\gamma_{LW}$ (mJ/m$^2$)</th>
<th>$\gamma^*$ (mJ/m$^2$)</th>
<th>$\gamma$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>57.1 ±2.6</td>
<td>5.1 ±1.5</td>
<td>0.2 ±0.1</td>
<td>36.8 ±2.6</td>
</tr>
<tr>
<td>formamide</td>
<td>61.5 ±7.4</td>
<td>25.2 ±1.5</td>
<td>17.3 ±1.1</td>
<td>43.0 ±1.0*</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>53.0 ±2.1</td>
<td>16.9 ±1.1</td>
<td>7.10$^4$±9.10$^{-3}$</td>
<td>0.5 ±0.3</td>
</tr>
<tr>
<td>dodecane</td>
<td>94.7 ±0.8*</td>
<td>16.9 ±1.2</td>
<td>7.10$^4$±8.10$^{-3}$</td>
<td>1.0 ±0.4</td>
</tr>
<tr>
<td>SS</td>
<td>57.1 ±2.6</td>
<td>44.6 ±1.5</td>
<td>16.9 ±1.2</td>
<td>41.6 ±4.2*</td>
</tr>
<tr>
<td>PFA-2</td>
<td>90.4 ±2.3*</td>
<td>16.9 ±1.2</td>
<td>7.10$^4$±9.10$^{-3}$</td>
<td>0.9 ±0.4</td>
</tr>
<tr>
<td>PFA-3</td>
<td>92.8 ±4.4*</td>
<td>19.3 ±9.6*</td>
<td>24.0 ±1.4</td>
<td>36.8 ±2.6</td>
</tr>
<tr>
<td>FEP-2</td>
<td>92.6 ±1.6*</td>
<td>20.2 ±0.1</td>
<td>11.1 ±1.5</td>
<td></td>
</tr>
<tr>
<td>PTFE-1</td>
<td>70.1 ±3.4*</td>
<td>0.2 ±0.2</td>
<td>0.5 ±0.3</td>
<td></td>
</tr>
</tbody>
</table>

*taken from Magens et al. (2017).

Fig. 5 Example of fouling monitoring record for a test on stainless steel. $\Delta P$ – left axis; mass flow rate and temperatures – right axis. Vertical dashed line at $t_1$ indicates when flow was changed from water to milk.

RESULTS

FLUOROPOLYMER PERFORMANCE

Fig. 6 shows the pressure drop evolution over time for all surfaces studied. PFA-2 showed fast accumulation of deposit and the experiments were stopped after 65 min. The pressure drop increased more slowly for PFA-3, but was growing quickly at later times and exceeded that of SS. FEP-2 performed better throughout. The performance of PTFE-1 is comparable to SS, nonetheless it shows a higher initial pressure drop which may be related to asperities formed by PTFE particles on its surface.

The mass of fouling deposit was determined after drying overnight and the data are presented as surface mass coverage in Fig. 7. There was significantly less deposit on the FEP-2 coated plates compared to SS, which is consistent with the $\Delta P$ results in Fig. 6. PFA-3 also accumulated less deposit, but gave a high pressure drop, suggesting that the deposit was more voluminous. The PTFE-1 coating accumulated a similar amount to SS, which is consistent with the $\Delta P$ data in Fig. 6. PFA-2 was not an effective coating as it accumulated a similar amount of deposit to the SS reference in half the time.

The photographs of deposits in Fig. 9 (a–e) show noticeable differences. On the polar surfaces (SS and PTFE-1), the layer is whitish and had a more brittle texture, indicating that it contained a larger amount of calcium phosphate. The deposit was firmly attached to SS, whereas on PTFE-1 it partly flaked off. On the non-polar surfaces, however, the deposit detached after the first seconds of drying at room temperature. This suggests that (i) drying causes shrinkage and tensions within the deposit; (ii) the cohesion of the dried deposit on non-polar surfaces is stronger than its adhesion; and (iii) adhesion is facilitated by the presence of water. Also, the deposit was more transparent and softer, suggesting a higher protein content.

While the deposits on the non-polar surfaces were easily cleaned, a strongly attached mineral layer remained on PTFE-1 and especially on SS after washing with 1M NaOH solution (see Fig. 9(f)). This layer was able to be cleaned with acid: here, 0.5 M H$_3$PO$_4$ was used.
CALCIUM AND PROTEIN DISTRIBUTION

CLSM was used to study whether the surface affects the composition of the deposit. Fig. 8 shows an CLSM section of the 120 min deposit on stainless steel. The channels indicating the presence of amines (a), calcium ions (b) and both (c) are shown separately. Blue indicates the amine groups in proteins and red the presence of Ca$^{2+}$ ions. The deposit appears generally uniform in composition, with some patches of variation parallel (lateral) to the surface.

In the asterisked region there are relatively more amine groups than calcium ions, suggesting a higher protein content. This variation is unlikely to arise from the surface, as it should only affect composition near the surface.

A higher resolution image, shown in Fig. 10, was taken with a 40× oil immersion lens ex situ, and confirmed spatial uniformity. At some points the fouling layer blistered.

Given the instantaneous changes in the fouling layers on non-polar surfaces when subject to drying, these were studied with CLSM in situ, i.e. without disassembling the fouling cell. Fig. 11 shows an example of a deposit cross section on PFA-3. The deposit layer was considerably thicker than on SS and the non-polar surface promoted the growth of a protein-dense layer extending up to 20 μm. The structure of the layer closely resembles those encountered around trapped air bubbles. An example of a bubble on SS is shown in Fig. 12. In contrast to the previous images, this scan was parallel to the surface. The accumulation of protein at the interface is evident: the protein acts as a surfactant.
Fig. 10 Orthogonal CLSM section of a fouling layer on SS. The channels for amine and calcium signals are shown individually in (a,b) and superimposed in (c). Image taken with 40× oil immersion lens ex situ.

Fig. 11 Orthogonal CLSM section of a fouling layer on PFA-3. The substrate is at the base and the solution above. Image taken with 10× air lens in situ.

Fig. 12 CLSM image, scanned parallel to the surface, of deposit on SS showing the cross section of an air bubble. Image taken with 40× oil immersion lens ex situ.

DISCUSSION
Pressure drop data and deposit mass coverage demonstrated that some fluoropolymers can mitigate raw milk HTST fouling compared to stainless steel. However, their antifouling effectiveness is influenced by their topology, with the smoothest coating (FEP-2) performing best. Considerable deposition occurred on all surfaces with bulk temperatures below 72 °C, (cf. Visser and Jeurnink 1997) indicating aggregation and chemical reaction in the hot boundary layer drove milk fouling.

Adhesion of a mineral-rich sub-layer, likely to be principally calcium phosphate, was strong after 120 min of processing at a surface temperature of 85 °C (see Fig. 9(f)). Hagsten et al. (2016), working with SS at higher temperatures and longer processing periods, also found a high calcium phosphate content at the surface. In contrast, the non-polar surfaces and air favoured protein adhesion. The range of influence of a material decays on the nanometre-scale (van Oss, 2003), suggesting that the affinity for low polarity or surface active species is propagated as the fouling layer grows.

The appearance and properties of the fouling layers was affected by the surface nature. Those formed on polar surfaces were noticeably more white, indicating a high mineral content. Those formed on non-polar surfaces were more transparent, loosely attached and detached partially on drying in air. The latter features indicate properties which could be exploited in tailored cleaning solutions (e.g. combined alkaline-chelant rather than two-stage alkali-acid), adding additional value to an antifouling coating by reducing cleaning times (see Magens et al., 2016).

CONCLUSIONS
1. A micro-scale heat exchanger system has been developed which allows the fouling behaviour of different surfaces to be studied. Its low liquid inventory facilitates work on microbially active liquids.
2. Tests on stainless steel and fluoropolymer coated steels showed that surface properties affected the nature and rate of fouling. The best antifouling performance was obtained with the smoothest fluoropolymer tested.
3. Polar surfaces favoured the deposition of mineral scale which also afforded strong adhesive characteristics to the fouling layers.
4. Deposits formed on non-polar surfaces had weaker adhesion than cohesive strength and the adhesion changed markedly on drying. Strongly non-polar surfaces (including air) favoured the formation of protein-rich layers.

ACKNOWLEDGEMENTS
A PhD studentship for OMM from Chemours and the provision of raw milk by the University of Cambridge Park Farm are gratefully acknowledged.

NOMENCLATURE
\[ A \] heat transfer area (mm\(^2\))
\[ a, b \] width, height of the channel (mm)
\[ D_h \] hydraulic diameter (mm)


