SURFACE TREATMENT FOR THE MITIGATION OF WHEY PROTEIN FOULING

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ABSTRACT

Heat transfer fouling experiments were carried out in a temperature controlled stirred vessel using aqueous solutions of whey protein concentrate in the concentration range of 3 to 3.5 wt-% at a bulk temperature of 50 °C and pH of 6. Heat transfer data were obtained from thermocouples embedded in an immersed electrical heating rod with various metal plates attached with-and-without surface treatments. Measurements included solution temperature, heating element surface temperature, and heat duty.

Results are presented as fouling resistance versus time for aluminum, copper, stainless steel, electro-polished stainless steel, and surfaces coated with DLC and doped with Si , SiO, as well as DLC-coating of an electro-polished stainless steel. Reducing surface roughness was found to mitigate fouling but the combination of both surface treatments, DLC coatings, and electro-polishing gave the best performance. The experimental results demonstrate the potential and value for reducing the adhesive behavior of whey protein fouling layers using modified surfaces. Also a comparison of these results with those for crystallization fouling show the same effects of the surface modification on nucleation and crystal growth. Of particular importance is the influence on the cleaning performance where the main potential can be expected.

INTRODUCTION

The formation of fouling layers during the thermal treatment of milk and milk products is a severe problem for the dairy industry. These layers can lead to a drastic increase in heat transfer resistance, thereby decreasing the thermal efficiency of equipment such as heat exchangers. Furthermore, the stringent requirements for quality and hygiene in dairy processes require regular and effective cleaning of production lines. Extra costs are thereby incurred for detergents, rinse water, disposal of spent solutions and energy.

A method to reduce fouling is the defined modification of interfacial interactions between heat transfer surface and deposit. These interactions are caused by molecular and mechanical forces, so two approaches for fouling mitigation have been developed:

• Modification of the energy related-properties of the heat transfer surface,

• Modification of the geometry-related properties of the heat transfer surface.

This work employs both strategies to reduce the fouling tendency and to promote efficient and effective cleaning.

The fouling process can often be divided into two periods, i.e. induction and fouling period, as shown in Fig. 1. One crucial parameter is the interfacial free energy between the protein and the heat transfer surface. For many industrial applications of heat exchangers the only possibility to influence this energy is the modification of energetic properties of the heat transfer surface, i.e. its surface energy.
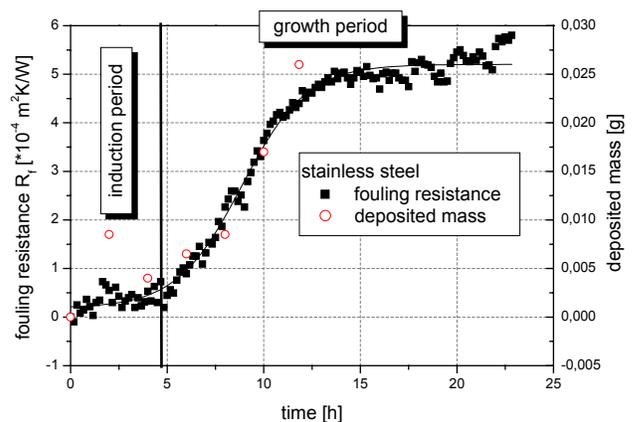
Fig. 1   Characteristic fouling curve (whey protein)

The fouling resistance, R_f, equation (1) was used for the determination of the deposited mass:

$$R_f = \frac{1}{k_f} - \frac{1}{k_0} \qquad (1)$$

The formation of first deposit on the heat transfer surface already takes place within the induction period. Subsequently, the profile of R_f can be measured as a function of time within the fouling period. The formation of an asymptotic end value depends on the process parameters. Both deposition and removal processes occur in the induction and fouling periods and a good correlation between the fouling resistance and the deposited mass is obtained as shown in Fig. 1.

As mentioned both deposition and removal processes occur in the induction and fouling periods and can be described by the deposition mass rate $\dot{m}_d$ and removal mass rate $\dot{m}_r$ (see Fig. 2). The fouling mechanisms in the induction period depend on the adhesion between the heat transfer surface and the deposit and whereas the deposition growth period is mainly influenced by the cohesion within the deposited layer.
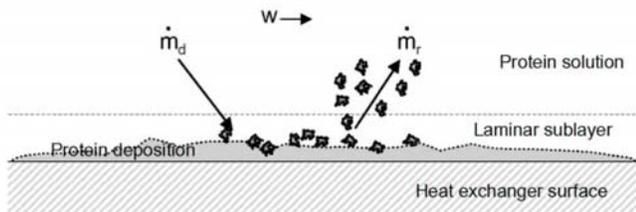
Fig. 2   Deposition and removal process

Modern anti-fouling strategies are based on approaches to increase the duration of the induction period and hence aim at decreasing the adhesive strength of the deposit (Förster et al., 2000). The interfacial interactions have to be analyzed in order to relate the physical properties of the interface deposit/heat transfer surface to adhesion (Zhao and Müller-Steinhagen, 2002).

Table 1 Performance appraisal of heat exchangers for different applications

Application	Performance appraisal of fouling
Cooling water	Heat duty and pressure drop
Chemistry	Product quality
Food	Hygiene
Pharmaceuticals	Sterility

Different requirements have to be taken in consideration depending on the application in technical processes (as listed in Table 1). In the chemical industry and for the cooling-water side, only the heat duty and pressure drop are relevant. On the product side, the product quality has to be considered carefully. In the food industry for example, the hygienic aspects are of great importance. In the pharmaceutical and medical sector, the sterility of the products is essential. The requirements of the process with respect to fouling lead to different prerequisites for the surface properties of the heat exchanger. Modified surfaces influence the interactions between substrate and deposit and can prevent or just mitigate fouling.

FUNDAMENTALS

Milk fouling

Milk is composed of water, fat, proteins, sugar, minerals and micro-organisms. The average percentage of proteins is 3.3%, with 2.6% casein and 0.7% whey. Burton (1968) classified milk fouling deposits as type A and type B, as shown in Table 2, with higher temperatures promoting the phosphate-rich, hard type B deposit.

Table 2 Classification of milk fouling deposits (Burton, 1968)

	Process parameters	Composition	Appearance
Type A	Pasteurization $T \leq 100°C$	Protein: 50-60% Minerals: 30-35% Fat: 4-8%	Soft and voluminous structure; white or cream-colored
Type B	Ultra-heat treatment $T = 110°C – 140°C$	Protein: 15-20% Minerals: 70% Fat: 4-8%	Brittle and porous; grey

Fig. 3   Whey protein fouling layer

The fouling layers generated from whey protein concentrate (WPC) solutions in this work exhibited type A characteristics (Gillham et al., 2000). Fig. 3 shows a photo of a whey protein-fouled heat transfer surface and a micrograph of the soft structure.

Robbins et al. (1999) compared deposits from milk and whey protein concentrate (WPC) for temperatures below and above 100°C. The SEM micrographs in Fig. 4 show a soft type A layer was formed for both substances at the lower pasteurization temperature. By comparison for the UH treatment the milk, the deposit is brittle and porous (type B), the WPC deposit has a protein-containing polymeric structure (similar type A). This indicates that WPC can be used as model fluid for the simulation of milk fouling, at least for pasteurization processes.
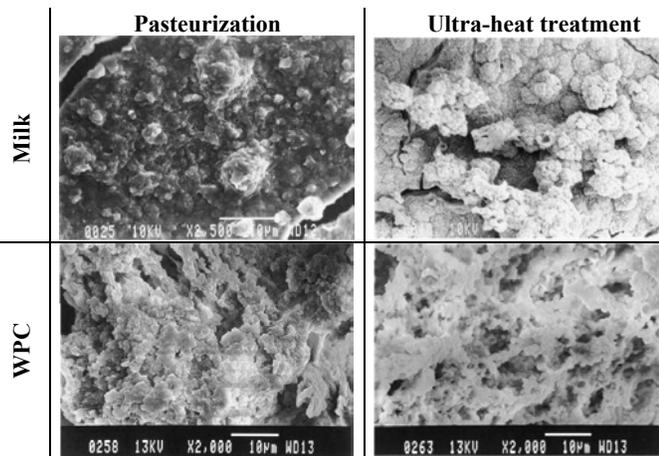
Fig. 4   Structure of the deposit of milk and WPC for different temperatures (Robbins et al., 1999)

Deposition of denatured proteins can be described as two successive processes: the adhesion of precipitated protein on a free surface (in this case the heat exchanger wall), and the growth of the layer by reactions between protein polymers. A higher rate of denaturation in the bulk can decrease deposition significantly (Dannenberg, 1986).

Grant et al. (1996) described a two- and a three-stage model for the deposition of milk on metal surfaces. In the induction period of the two-stage model, a thin layer of salts and proteins is formed on the surface. In the fouling period insoluble protein aggregates are formed by denaturation in the bulk solution. These aggregates adhere to the deposit layer formed in the induction period, causing the deposit to grow (Sandu, 1989). In the three-stage model (see Fig. 5) the compact sublayer composed of calcium phosphate and proteins is formed at the heat transfers surface.
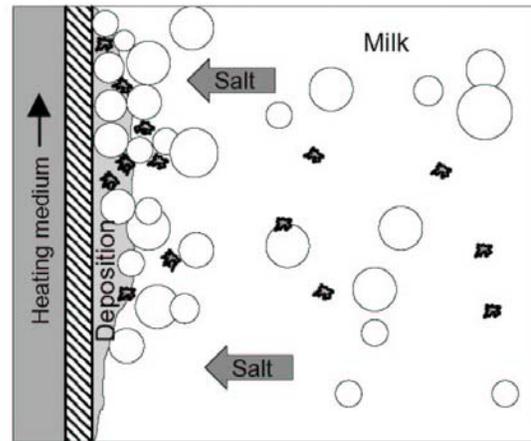
Fig. 5   Three-stage model of milk fouling (after Gotham et al., 1989)

Some active sides on the sublayer surface provide anchors for the granules of large protein aggregates, leading to a growth of a porous, spongy deposit with low density and high moisture content (Gotham et al., 1989). No final conclusion as to which model is actual relevant for the milk fouling process is presented in the research literature. It is assumed that the three-stage model is characteristic for the deposition process in this work because of the types of comparisons as shown in the micrograph in Fig. 4.

Surface modification
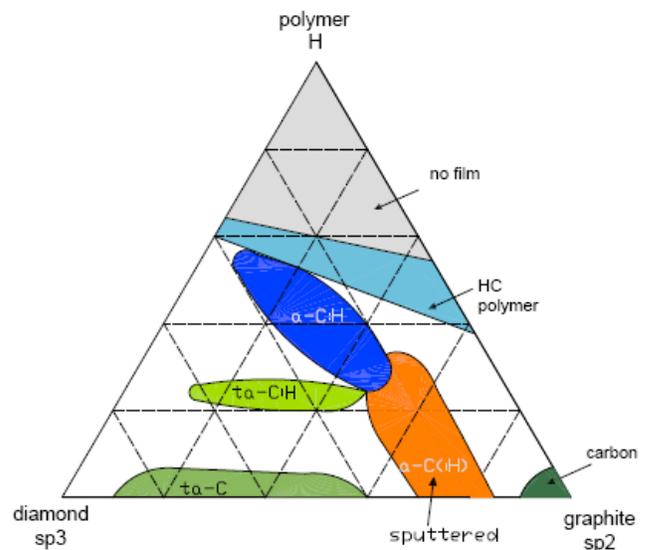
Fig. 6   a-C:H (DLC) in the carbon phase-diagram triangle

Amorphous carbon hydrogen (a-C:H) also called diamond like carbon (DLC) is a common coating used to enhance wear resistance and surface hardness. In the phase-diagram triangle of diamond, graphite and polymer (see Fig. 6), the surface characteristics of a-C:H coatings can have different rates of polymer, diamond or graphite interactions (Trojan, 1996).

Stainless steel was coated with amorphous carbon-hydrogen layers by plasma-enhanced chemical-vapor deposition (PECVD) in a high-vacuum chamber to modify the energetic properties of the heat transfer surface. The thickness of the coating was 3 µm and consequently the influence of this additional layer compared to the uncoated surface on the heat transfer was negligible. The chamber was evacuated to a base pressure of $<10^{-3}$ Pa. Before starting the DLC deposition the substrates were cleaned by sputtering with Argon ions for a few minutes. To achieve good adhesion, a silicon-containing DLC interlayer (a-C:H:Si; some 100 nm thick) was prepared using tetramethylsilane (TMS: $Si(CH_3)_4$) as a precursor gas. In the next step the gas composition was changed to pure hydrocarbon gas, methane (CH_4) or acetylene (C_2H_2) for pure DLC films, and in some cases TMS or hexamethyldisiloxane (HMDSO). The PECVD process ensured a surface coating where roughness as well as topography were only marginally changed.
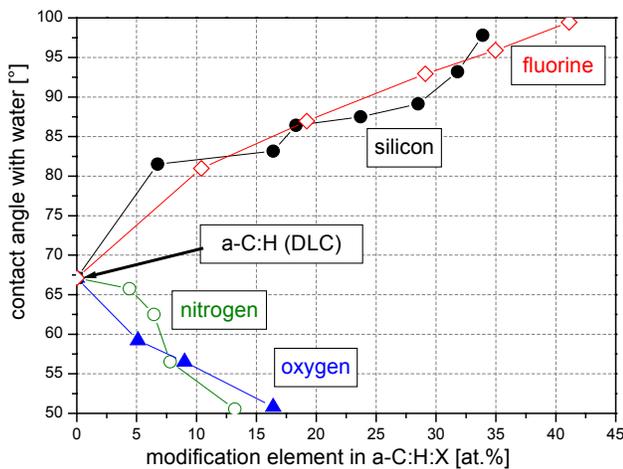
Fig. 7   Water contact angle of DLC-based coatings

The surface energy or contact angle can be reduced significantly by the defined built-in of different elements in the a-C:H matrix like silicon and oxygen (a-C:H:Si:O) or fluorine (a-C:H:F) which are both hydrophobic and oil repellent. Fig. 7 shows the water contact angle as a function of different molecules and concentration inside the a-C:H

layer. Low surface energies correspond to high contact angles. The increase of silicon inside the matrix can change the surface energy from 40 mN/m (DLC) to 36 mN/m (Si-DLC with 15 at.% Si) and finally to 34mN/m (SICAN® with 33 at.% Si). Silicon and oxygen modified DLC (SICON®) can reduce the surface energy to 22 mN/m.

EXPERIMENTS

Experimental set up

Fouling experiments were carried out in a temperature controlled 2.8 l stirred vessel as illustrated in Fig. 8. A slowly rotating stirrer equalized the temperature and concentration gradients. Aqueous solutions of whey protein concentrate (WPC) with concentrations of 3 and 3.5 wt-% and a bulk temperature of 50 °C were prepared. The pH-value was set at pH 6 with 0.1 molar hydrochloric acid. The concentration was quantified with the modified Bradford assay described by Gillham *et al.* (2000), which is a photometric method employing Coomassie Blue dye as an indicator.
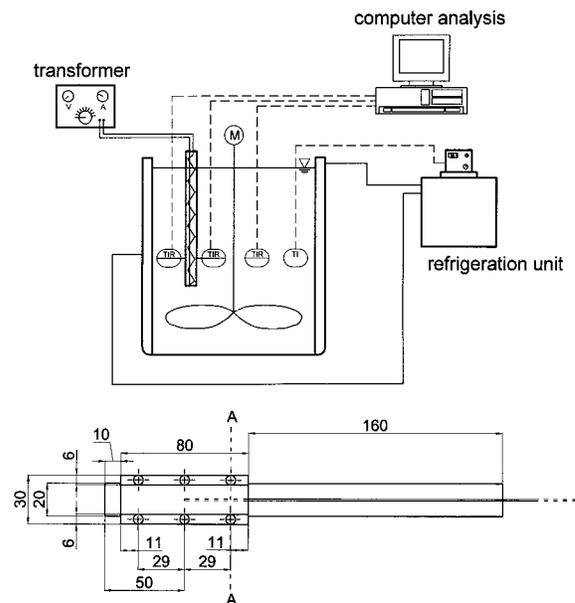
Fig. 8   Test rig and heating element

An electrical rod was immersed in the whey protein solution. Two 1 mm diameter thermocouples were fixed in machined grooves on two sides of the heating element. The actual heated plates with the different surfaces were clamped with brackets on the two sides with the

thermocouples. This allowed for a simple design (80 mm × 20 mm × 2 mm) and an easy assembly of the test items. The surface temperature was adjusted between 70 - 80 °C.

The measured quantities were: solution temperature, surface temperature of the heating elements, and heat duty. The fouling resistance was determined from the change in temperature difference between the bulk and the surface over time.

Surface characterization

The macroscopic roughness as well as surface topography were investigated in order to characterize the heat transfer surface before scaling. In addition to the mechanical surface properties, energetic properties like surface energy were measured to evaluate the success of the coating process and investigate the interrelations between surface energy, roughness and fouling tendency. Förster et al. (1999 and 2000) and Zettler et al. (2005) negated a direct correlation between surface energy and fouling tendency in the induction time, while most authors associated an decrease of roughness with an increase of the induction time.

Surface roughness was investigated with a macroscopic tactile stylus unit. For the evaluation of surface contour, the R-profile (roughness profile) was deployed which was obtained from filtering the original P-profile (primary profile). Fig. 9 shows the mean roughness depth of the tested coatings. Stainless steel was the roughest substrate material and was smoothed by electro-polishing. For surfaces coated by PECVD, the mean roughness depth was nearly constant, so the effect of roughness on the induction period was regarded as negligible.
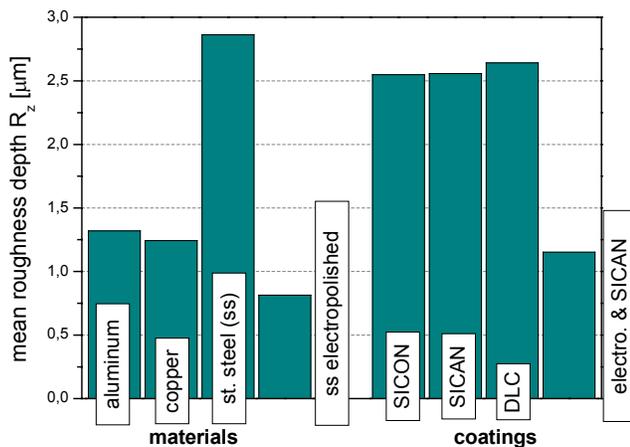
Fig. 9   Surface roughness

To characterize the different energetic modification through PECVD coatings, surface energy was measured with the sessile drop technique. The surface energy should replace the adhesion which should be minimal for optimized process conditions (Dyckerhoff, 1972). The principle is based on the measurement of the shape of droplets of different defined liquids. A more detailed description of the surface energy measurement can be found in Förster (1999).

Fig. 10 shows the influence of the 3 μm coated layer on the free surface energy. All surface energy measurements were done with plates already used in fouling experiments to simulate real process conditions. The coating with a-C:H:X tends to advance the polar part of the surface energy when compared with the untreated stainless steel surface. Using the defined doping of silicon inside the DLC matrix, the surface energy can be reduced (SICAN). A combination of oxygen and silicon inside the coating leads to a further decrease of the surface energy (SICON®). Interesting is the effect of electropolishing before coating with DLC. The polar part and thus the overall surface energy is reduced significantly.
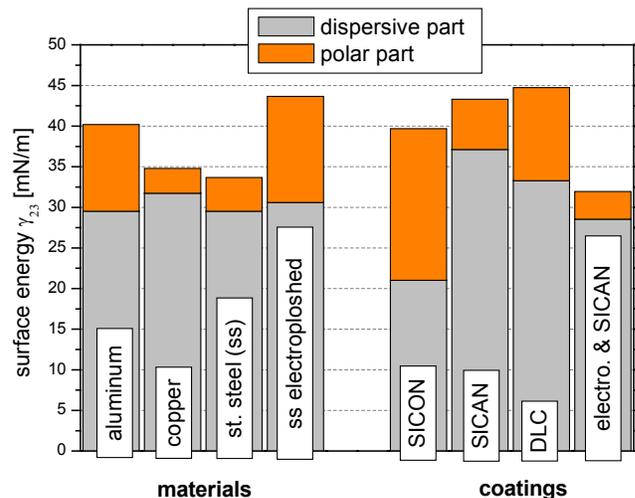
Fig. 10   Free surface energy

Sample plates were stored in 0.1m aqueous sodium hydroxide solution at ambient conditions for 24 h to investigate the potential effect of aging of the coatings on surface energy. As shown in Fig. 11, the treatment with NaOH (simulating the CIP of equipment in the dairy industry), causes only a small change of surface energy for stainless steel which is only due to the increase of the dispersive part. For the DLC-coated probes the shift is much larger as it attracts only the polar part. The Si- and SiO-

doped surfaces both show an even higher increase of the overall surface energy which again is caused by the increase in the polar part. The value of the dispersive part is nearly constant. A small increase can be observed only for SICON[®]. With Secondary Ion Mass Spectrometry (SIMS), an inclusion of oxygen in the first atomic lattices could be detected which may effect the free-surface energy. This investigation showed that for realistic results analysis data from unused surfaces can be disregarded.
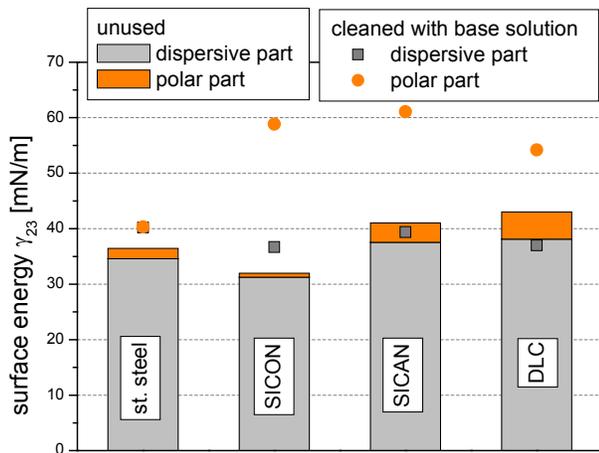
Fig. 11   Aging of surfaces after treatment with NaOH

Fouling runs

The operating conditions of temperature and concentration were first varied using the stainless steel probes.
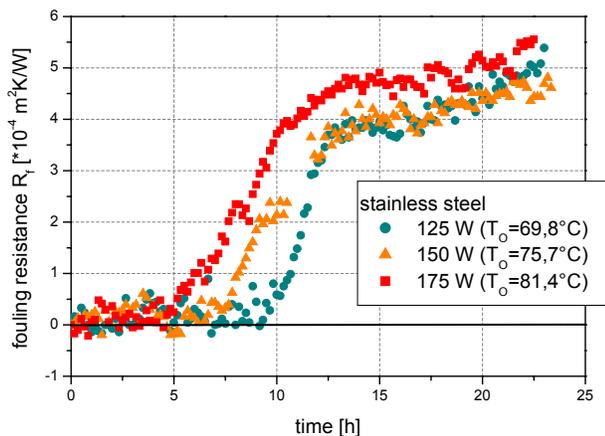
Fig. 12   Fouling curves for different surface temperatures

As shown in Fig. 12, the increase of the surface temperature reduces the induction time due to the soaring denaturation of the whey protein at temperatures above approximately 70°C. Once the growth of the deposit had started, the slopes of the fouling curves were identical.

In Fig. 13 the influence of the whey protein concentration is illustrated. While for a concentration of 3 wt-% the induction period still existed after 24 h. Increasing the concentration to 3.5 wt-% caused a rapid growth of the deposit already after 5 h and an increase in fouling rate (slope). For the further experiments the concentration of 3.5 wt-% was adjusted.
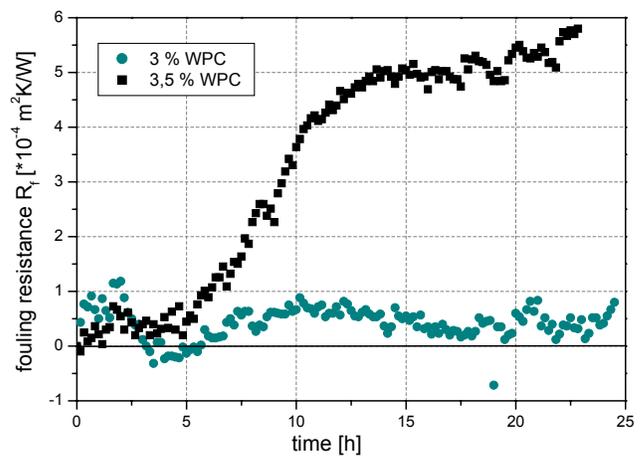
Fig. 13   Fouling curves for different whey protein concentrations
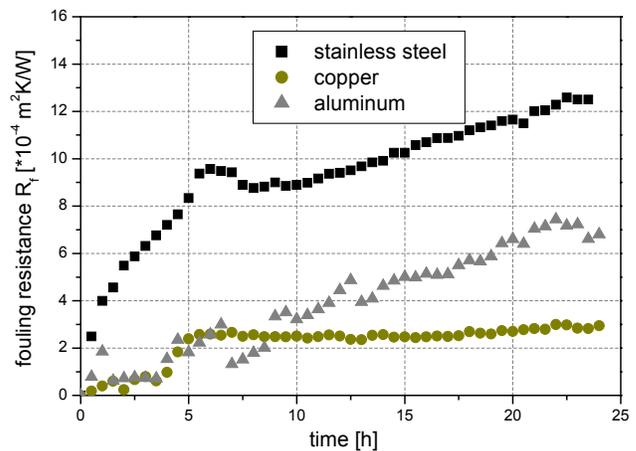
Fig. 14   Fouling curves for different substrate materials (T_{bulk} = 40°C)

Fig. 14 shows fouling curves for different metallic surfaces. For stainless steel the growth of the deposit starts immediately subject to the process conditions. Copper and aluminum have induction times of approximately 4 h. When fouling starts for the aluminum surface the slope of the curve and therefore the growth of the layer over time is comparable to stainless steel. The fouling curve for cooper reaches a low asymptotic value after a short growth period. Copper as a biologically active material is apparently inhibiting the adhesion of the denatured protein from the bulk with the already deposited material. This influence is even effective through the thin protein layer whereas the growth period is not influenced by the nature of the other materials.
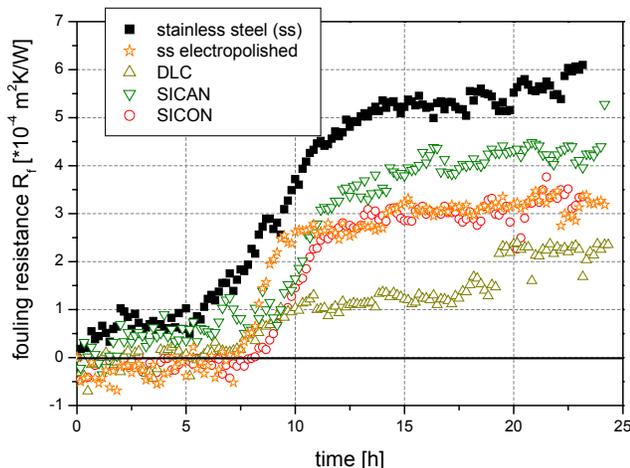
Fig. 15   Fouling curves for different coated surfaces

The fouling curves for the different coatings employed are displayed in Fig. 15 and compared with the untreated and electropolished stainless steels. There is a difference in the length of the induction period of between 5 h for stainless steel, and 8 h for electropolished stainless steel and SICON®. DLC and SICAN treated surfaces reached intermediate values for the induction time. The slope of the fouling curves is similar for all materials except DLC. The effect of the substrate material (as shown for copper in Fig. 14), was also observed by Augustin et al. (2006) for crystalline deposition. Thus both nucleation and crystal growth were influenced by the nature of the surface.

In Fig. 16 a SICAN-coated electropolished surface is compared with reference measurements. A SICAN-coated and an electropolished stainless steel surface individually improved the fouling behavior. The combination of both surface treatments resulted in the best performance. This collaborated the hypothesis that surface energy and

topography have to be taken into consideration jointly with respect to fouling behavior.
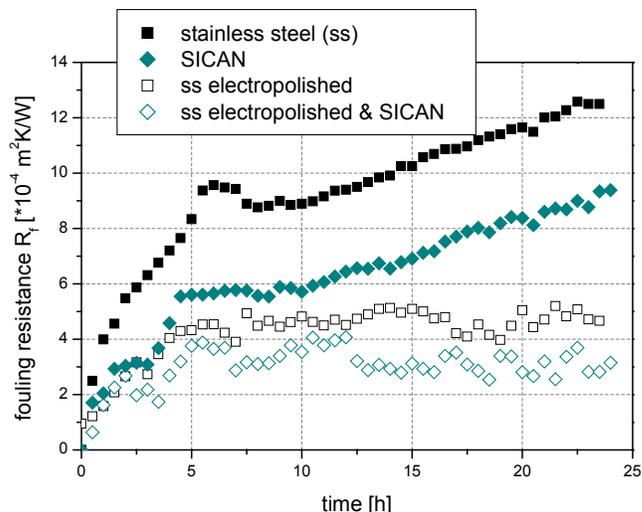
Fig. 16   Fouling curves for different modified surfaces (T_{bulk} = 40°C)

A possible explanation for the effect of surface energy on the induction period is given in Fig. 17. Here the differently treated surfaces investigated are listed with ascending induction time. Concurrently the polar part of the surface energy is increasing. It appears that molecular interactions and forces between the polar surface and the active parts of the protein deposit are significant.
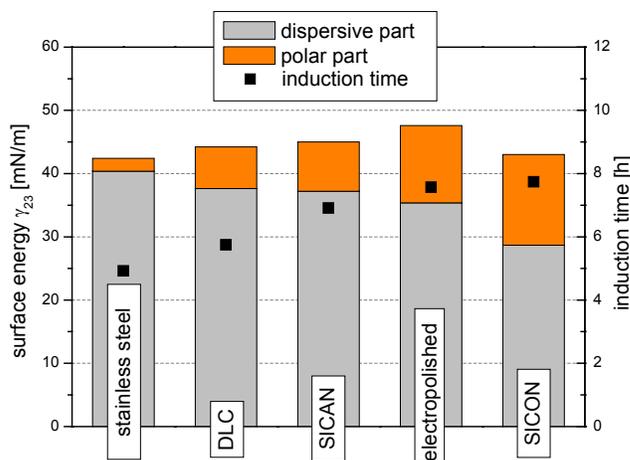
Fig. 17   Free surface energy and induction time of different coated surfaces

CONCLUSIONS

The experimental results illustrate the potential for reducing the adhesive behavior of whey protein fouling layers by the application of modified surfaces. The fouling resistance can be reduced by the application of DLC-coated surfaces due to the change of surface energy. Also a reduction of surface roughness by electopolishing can mitigate fouling. The combination of both surface treatments, DLC-coating of an electropolished stainless steel surface, results in the best performance.

Reviewing all the results indicate that the free-surface energy as well as the topography affect the fouling process. Thus the polar part of the surface energy is of great importance for the protein system investigated and clearly demonstrates the potential of surface modification. The aging of the surface properties has to be taken into account for the design of tailored surfaces.

A comparison of these results with those for crystallization fouling show the same effects of the surface modification on nucleation and crystal growth. If the deposition takes place according to the three-stage model, the mitigation of the first crystal layer is the explanation for the overall improvement of the fouling behavior. The understanding of the physical and chemical interactions between surface and deposit, *i.e.* its impact on adhesion, is a crucial premise for the development of a comprehensive model describing the fouling process.

ACKNOWLEDGEMENTS

NOMENCLATURE

k_0	heat transfer coefficient (clean surface), $\mathrm{W\,m^{-2}\,K^{-1}}$
k_f	heat transfer coefficient (fouled surface), $\mathrm{W\,m^{-2}\,K^{-1}}$
$\dot{m}_d$	deposited mass flow, $\mathrm{kg\,s^{-1}}$
$\dot{m}_r$	removed mass flow, $\mathrm{kg^{-1}}$
R_f	fouling resistance, $\mathrm{m^2\,K\,W^{-1}}$
R_Z	mean roughness depth, m
T	Temperature, K
t	time, s
w	velocity, $\mathrm{m\,s^{-1}}$
γ_{23}	free surface energy, $\mathrm{N\,m^{-1}}$

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