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BIOMIMETIC COATINGS TO MITIGATE DAIRY FOULING ADHESION

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ABSTRACT

In dairy industries, production costs are highly impacted by the deposition of fouling onto equipment. Promising coatings to prevent fouling adhesion (*i.e.* anti-fouling) or to ease fouling removal (*i.e.* fouling-release) were previously developed. Nonetheless, their durability and food-compatibility were limited. Consequently, to overcome these limitations, this work aims at designing biomimetic coatings based on innovative surface modification techniques and concepts: (*i*) polymer deposition by atmospheric pressure plasma (APP) torch and (*ii*) slippery surfaces by femtosecond laser ablation and oil infusion. The first technique allowed the successive deposition of hexamethyldisiloxane (HMDSO) and 1H,1H,2H,2H-perfluorooctyltriethoxysilane (pFOTES) leading to ultra-hydrophobic and very stables bilayers. Promising fouling-release performances were obtained allowing to reduce dairy fouling (type A, mainly composed of proteins) up to 72%. The second research axis consisted in designing slippery liquid-infused surfaces (SLIS) following three steps: (i) laser structuration of stainless steel, (ii) chemical modification of structured surface and (iii) lubricant impregnation. An optimization of laser parameters allowed to reach quickly various types of deep microstructures. Food-compatible SLIS were developed by replacing fluorine-based lubricant by coconut oil. A dairy fouling reduction of 100% was reached using coconut-SLIS, highlighting excellent fouling-release properties.

INTRODUCTION

Fouling is usually described as the accumulation and attachment of unwanted materials at the surface of industrial equipment or devices. In dairy industries, milk pasteurization is mandatory to prevent food contamination by microorganisms and to increase the food shelf life [1]. However this thermal treatment also induces fouling formation onto plate heat exchangers (PHE) impairing heat transfer mechanisms and facilitating the proliferation of bacteria and biofilm. Regular cleaning of PHEs are thus required. Consequently, the stakes of fouling mitigation are mainly economical ones, since it has been estimated that 80% of production costs are owed to dairy fouling deposit [2]. Förster *et al.* proposed pathways to mitigate dairy fouling adhesion either by optimizing process parameters or by modifying stainless steel (SS) surface [3]. As the optimization of process parameters remains complex to perform at laboratory scale, we focus on SS surface modification using innovative techniques to develop biomimetic coatings: (i) lotus-like nano-structured plasma bilayers and (ii) fluorine-free slippery liquid-infused surfaces.

1. FOULING-RELEASE PROPERTIES: PASTEURIZATION TEST

In this study, fouling-release properties of biomimetic were assessed using a pasteurization test. The model fluid was composed of a 1% of WPC solution and a 100 ppm of $CaCl_2$ solution. For each pasteurization run 500 L of model fluid was prepared. Reference and modified stainless steel substrates were placed in a sample-holder, connected at the outlet of the heating section (85°C). The model fluid was circulated at 300 L/h for 60 min onto samples, then a 20 min-hot water rinsing (85°C) was performed to assess fouling-release performances. Samples were taken out of the sample-holders, dried in a cold room at 4°C for 5 days and then weighed and compared to bare stainless steel surfaces. At least three tests were performed for each type of surface.

2. NANO-STRUCTURED PLASMA BILAYERS

Nano-structured bilayer coatings were deposited onto SS samples by APP [4]. The bilayer

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(HMDSO/pFOTES) was characterized and compared to both HMDSO and pFOTES single layers. First, ToF-SIMS analyses were carried out to validate the formation of a bilayer resulting from the successive deposition of HMDSO and pFOTES. **Figure 1** displays resulting depth profile with post-processing of depth profile data allowing to obtain 2D reconstructions in x-z directions. These results highlight the presence of a fluorine-based layer, located at the outer surface (F^- and SiO_2F^- fragments) and the presence of a second siloxane-based layer (SiO_2^- fragment), thus confirming the deposition of a bilayer by APP torch.

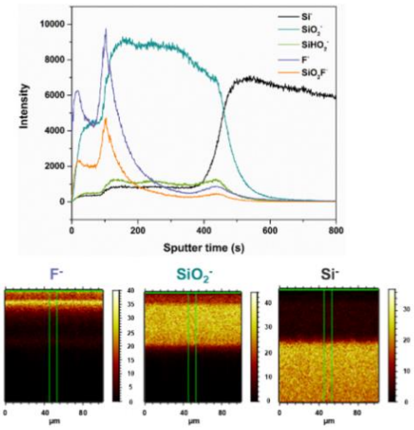

Fig. 1. ToF-SIMS depth profile of HMDSO/pFOTES plasma bilayer onto silicon wafer and 2D reconstruction (x-z direction) of the bilayer.

According to the literature to minimize fouling adhesion, surfaces should have a very low roughness (Ra < 60 nm) and a low SFE (20 and 30 mN/m) [5]. Consequently, surface properties of both single layers and bilayer were analyzed. Surface roughness was assessed using a profilometer and wettability were analyzed using a goniometer to calculate SFE.

Table 1. Surface properties of HMDSO and pFOTES monolayers and bilyer.

Surface properties	HMDSO	pFOTES	Bilayer
WCA (°)	107.7 ± 3.1	138.1 ± 3.4	Super-hydrophobic
SFE (mN/m)	19.2 ± 0.3	4.0 ± 0.0	N/D
R_a (nm)	38 ± 2	43 ± 2	38 ± 3

As observed in **Table 1**, all coatings have a roughness lower than 60 nm. However, HMDSO layer has a SFE close to the targeted range. Regarding pFOTES layer, SFE is very low due its surface chemistry (CF_x groups). It was not possible to calculate SFE for the bilayer due to its superhydrophobicity, water was completely repelled from the surface.

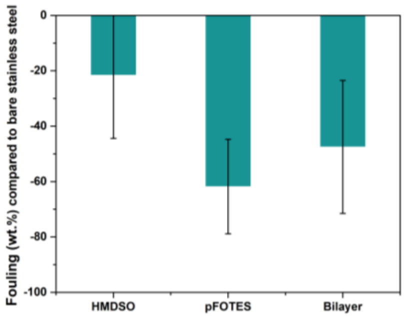

Fig. 2. Fouling-release performances HMDSO and pFOTES single layers and HMDSO/pFOTES bilayer.

Both single layers (HMDSO and pFOTES) and bilayer were then submitted to a pasteurization run of one hour followed by a hot water-rinsing for 20 min. Fouling-release performances are displayed in **Figure 2**. Although HMDSO/pFOTES was ultra-hydrophobic, it was slightly less efficient than pFOTES monolayer to reduce fouling deposit: 54 ± 24% against 65 ± 17% respectively. This can be explained by the presence of larger aggregates in HMDSO/pFOTES bilayer (**Figure 3**) making the surface rougher, which could favour the attachment of native whey proteins and calcium clusters.

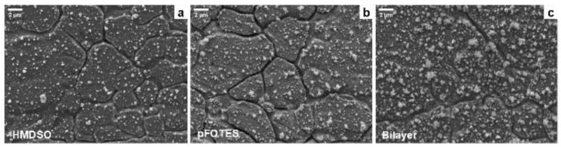

Fig. 3. SEM images of HMDSO (a.) and pFOTES (b.) single layers and HMDSO/pFOTES bilayer (c.).

In order to reduce the formation of large nanoparticles, the influence of plasma power on the bilayer deposition was studied. Indeed, Massines *et al.* highlighted that the power decrease can limit the precursor fragmentation and thus the formation of large nanoparticles [6]. As observed in **Figure 4**, the lower the power the less the aggregates on the bilayer.

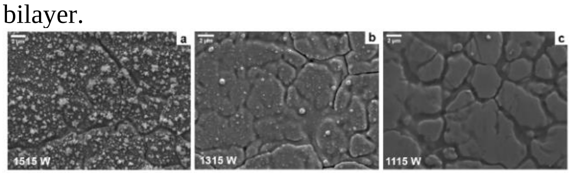

Fig. 4. SEM images of HMDSO (a.) and pFOTES (b.) single layers and HMDSO/pFOTES bilayer (c.).

The resulting fouling-release performances are shown in **Figure 5**. Although standard deviations are important, it seems that the fouling deposit slightly decreases with the power. The bilayer deposited at low power (*i.e.* high frequency) shows a fouling deposit reduction of 72 ± 20 % while a reduction of 48 ± 24 % is obtained for the bilayer deposited at high power.

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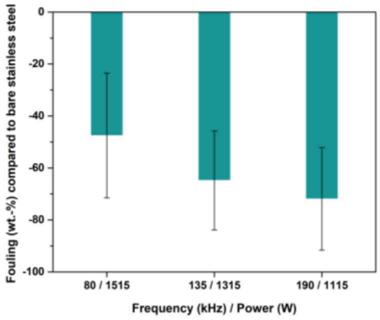

Fig. 5. Fouling-release performances of plasma bilayers as the function of power.

In the literature SiO_x plasma coatings are deposited with under vaccum systems [5]. Therefore, although, plasma bilayer coatings were not able to ease completely fouling removal, APP is a promising technique as it could be put in production line.

3. FLUORINE-FREE SLIPPERY LIQUID INFUSED SURFACES

Most of SLIS are usually infused by fluorinated-based lubricants, which are no longer food-compatible [7]. Therefore, the aim of the study was to replace fluorinated-lubricant to mitigate dairy fouling adhesion. Coconut oil seems suitable to replace fluorinated oil as it has a very low interfacial tension (18 mN/m) and is not part of allergen foods [8]. SLIS were produced following either two or three steps as illustrated in **Figure 6**. The two-steps protocol consists in: *(i)* femtosecond laser-structuring stainless steel and *(ii)* lubricant impregnation. The three-steps protocol was based on the method develop by Zouaghi *et al.* gathering: (*i*) femtosecond laser-structuring stainless steel, (*ii*) chemical modification (silanization) and (*iii*) lubricant impregnation [9].

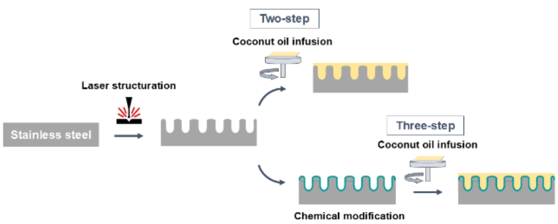

Fig. 6. SLIS process fabrication workflow.

In order to maximize the volume of infused coconut oil, an optimization of laser manufacturing parameters was performed. Laser fluence and overlapping rate (TO) were investigated. The first parameter corresponds to the delivered energy per surface unit while the second one corresponds to the distance between two scan lines.

Figure 7 a and b shows the impact of laser fluence on structuration. The high fluence allowed to obtain chaotic structures with deep valleys (characterized by profilometry through R_v parameter) , which are more suitable to maximize the volume of infused oil. Therefore the fluence was fixed at 11 J/cm². Then the overlapping rate (**Figure 7 c and d**) was varied between 0 and 50% leading to either a grid-like organization or a maze-like organization. The maze-like organization has deeper valleys (R_v: 15.1 ±1.8 µm) than the grid-like one (R_v: 9.8 ± 3.3 µm), thus the maze-like was used for the SLIS fabrication.

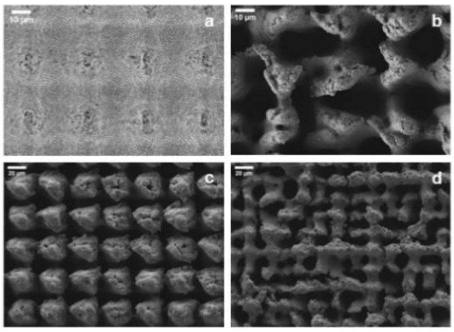

Fig. 7. SEM images of structured stainless steel surfaces: a. Low laser fluence (1.1 J/cm²), b. High laser fluence (11 J/cm²), c. No overlapping (TO: 0%) and d. With overlapping (TO: 50%).

Prior to coconut oil infusion, structured stainless-steel samples were then either unmodified or chemically modified through different techniques: *(i)* OTS by silanization, *(ii)* carnauba wax by spray coating and *(iii)* HMDSO by APP. A silanization of stainless steel is usually performed to insure a good affinity between the substrate and the lubricant [10]. In order to make SLIS fabrication process industrializable, carnauba wax and HMDSO.

The four different surfaces were submitted to two pasteurization runs of one hour followed by a hot water-rinsing for 20 min. Fouling-release performances are displayed in **Figure 8** (1st use in green and 2nd use in orange). After the 1st run, OTS, carnauba wax and HMDSO modified samples allow to reduce partially fouling deposit (deposit weight reduction of 79 ± 32%, of 54 ± 7% and of 69 ± 50 wt.-% respectively), while unmodified SLIS show promising fouling-release performances (deposit weight reduction of 114 ± 19%). For some samples, fouling reduction was higher than 100%. This is likely related to coconut oil loss during the fouling test. This result highlights also that the chemical modification step is not mandatory when coconut oil is infused, making SLIS fabrication process faster.

The second pasteurization run demonstrated that the remaining volume of infused coconut oil was not sufficient to reach good fouling-release performances.

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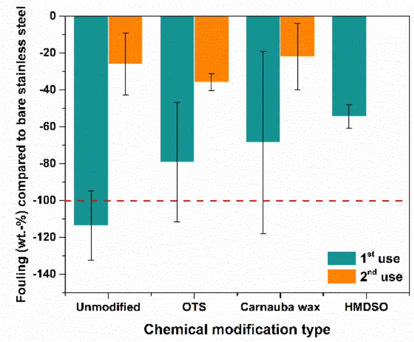

Fig. 8. Fouling-release performances of coconut-based SLIS for the 4 different surfaces after the 1st (green) and the 2nd use (orange).

The durability of SLIS were not improved however, this study demonstrated the possibility to make SLIS fabrication process faster. Moreover the use of coconut oil seems to be promising for food application. Indeed, fluorine-based lubricants are usually used to design SLIS [9].

CONCLUSION

The aim of this work was to develop biomimetic coatings to mitigate dairy fouling adhesion using innovative surface modification techniques.

In a first part, ultra-hydrophobic bilayer coatings were successfully deposited onto SS samples. The bilayer was less efficient (48 ± 24%) to ease fouling removal than the fluorine-based monolayer (62 ± 17%), likely due to its complex morphology (nanoparticles and large aggregates). Nevertheless, the decrease of power allowed to reach a fouling deposit reduction of 72 ± 20%. At low power the resulting bilayer showed a smooth surface (*i.e.* without nanoparticles or aggregates). Further plasma parameters optimization has to be done to enhance the effectiveness of superhydrophobic bilayer plasma coatings as well as tests to assess the durability of the coatings.

In a second part, SLIS fabrication process was optimized: (*i*) laser fluence and overlapping rate to maximize the volume of infused oil, (*ii*) several chemical modifications and (*iii*) replacement of fluorinated-based lubricant. High laser fluence (11 J/cm²) and high overlapping rate (50%) led to deep structuration more suitable to increase oil retention. Among the different chemical modification types, unmodified SLIS showed promising fouling-release performances, with a fouling (deposit weight reduction of 114 ± 19%), emphasizing that coconut-based SLIS can be fabricated in two steps, making SLIS fabrication process faster.

Regarding industrial application, these two types of process have their advantages and drawbacks. The deposition of plasma coatings is very fast and can be easily be put in place on a production line. However the results were slightly less promising than the ones obtained with SLIS samples. Regarding SLIS fabrication, laser structuration step is long, however, SLIS could reuse numerous time by circulating hot coconut oil to refill structured surfaces. Indeed Zouaghi *et al*. demonstrated that SLIS showed excellent fouling-release performances with a lubricant refill between two pasteurization tests [9].

LIST OF ABBREVIATIONS

APP: Atmospheric pressure plasma
HMDSO: Hexadimethylsiloxane
OTS: Octadecyltrichlorosilane
pFOTES: 1H,1H,2H,2H-perfluorooctyltriethoxysilane
PHE: Plate heat exchanger
R_a: Arithmetic mean deviation of the profile
R_v: Maximum profile valley depth
SFE: Surface free energy
SLIS: Slippery liquid-infused surface
TO: Overlapping rate
ToF-SIMS: Time of flight secondary ion mass spectroscopy
WCA: Water contact angle
WPC: Whey protein concentrate

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