Colloids and Surfaces A: Physicochem. Eng. Aspects 498 (2016) 268–275

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Tribological influence of a liquid meniscus in human sebum cleaning

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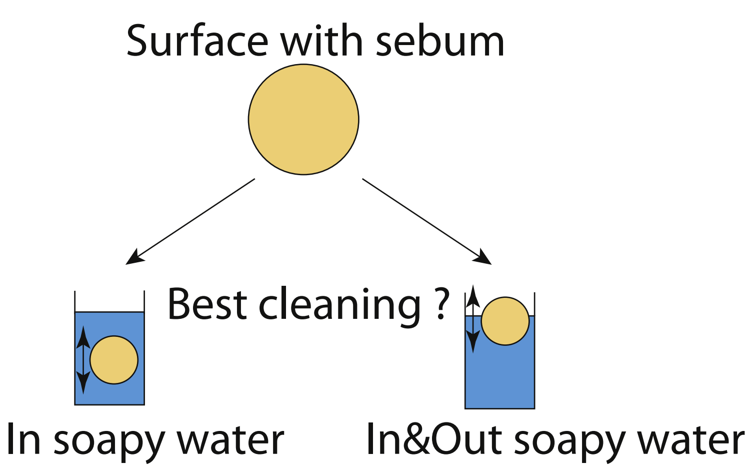
HIGHLIGHTS

- Silicon wafers are used as model surfaces for tests to measure the removal of a model lipid mixture.
- The presence of gas-liquid interfaces in the cleaning medium enhances the cleaning efficiency.
- Changing the surface energy of the wafer has a very strong effect on the cleaning efficiency.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 February 2016
Received in revised form 15 March 2016
Accepted 17 March 2016
Available online 24 March 2016

Keywords:
Detergency
Foam-oil interaction
Surface energy

ABSTRACT

The interaction of surfactants in solution with hydrophobic materials is at the root of the process of detergency. Lipid containing micelles are formed in solution, and through water rinsing, these structures are washed out from the surface. The presence of air in the solution and the formation of foam add complexity to the system due to the increased proportion of water interfaces in contact with the surface. The latter situation is more difficult to understand. In this work, we propose, as a first step, to explore the role of the interfaces in cleaning silicon wafers previously coated with a model lipid mixture representing human sebum has been investigated. It turns out that the presence of interfaces enhances the cleaning efficiency. The effect of altering the surface properties of the silicon wafer was also investigated and it was found that changing the contact angle of the wafer brought a very strong effect on the cleaning efficiency.

1. Introduction

Human sebum is excreted at the skin surface through hair follicle ostia by the sebaceous glands, present in specific areas of the body. Its composition differs from most other excreted fluids that

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http://dx.doi.org/10.1016/j.colsurfa.2016.03.047
0927-7757/

are water based, such as sweat, since lipids comprise the majority of its components [1,2].

The amount of surface sebum depends on many factors (area of the body, age, gender, ethnics, time, *etc.*). Its presence is usually associated with the appearance of secondary effects that, despite not being pathogenic, induce unpleasant sensations such as greasiness, stickiness, excessive shine, *etc.* which are important from a hygienic but also aesthetical point of view. In dermatology and cosmetics, excess of sebum is associated with many skin disorders (acne, dandruff...). Bacteria may also proliferate, often giving rise to odors [3].

Sebum is also present on hairs coming from the scalp hair follicles and extending from the root through capillary forces [4]. Together with a variety of solid pollutants that adsorb onto the hair with time, sebum is the target for shampoos designed specifically to clean, restore or improve hair's natural (native) properties. Hair structure is complex and its outer surface is itself covered with covalently linked fatty acids that impart a hydrophobic character [5]. Exposure to UV, weathering and oxidative treatments partially or even completely remove this lipid layer by creating sulfonic groups as a result of oxidative disruption of keratin cystine linkages making hair more hydrophilic [4].

Surfactants are the core ingredients of shampoos to eliminate the excess of sebum as detergency is the classical mechanism used for hair cleaning. The detergency process is based upon different physical mechanisms such as roll-up or micellar solubilization (classic detergency) and further removal of dirt from surface by dispersion and surface water rinsing [6–8].

In the "rolling up" mechanism, the oily sebum phase initially spreads onto the hydrophobic surface of hair. Hair is then progressively wetted by the surfactant-containing aqueous solution. The droplets of sebum are coated by the surfactant and subsequently detached from the surface. Other mechanisms also play a role. For example liquid sebum can dissolve into the surfactant micelles (micellar solubilization) but micelle's removal capacity is limited due to the low surfactant/sebum ratio in solution. In addition, the dispersion of the oily phase in small droplets is important. The shampoo surfactants help maintaining this dispersion. In the case of sebum, the presence of amphiphilic substances (*i.e.* fatty acids or proteins) can promote its dispersion although not up to a satisfactory level [4].

A general consensus exists among specialists of detergency that any foam generated during washing, whether of clothes or hair or skin, does not take an active part in the cleaning process. It is acknowledged that the production of smooth, creamy foam has a strong psychological effect on the user, and that foam also improves spreading and coverage of hair and skin, but in overall foam is usually considered only as a side product of the surfactant used for cleaning. This is discussed, for example, in reference [9], which quotes Roland Barthes, who says that "what matters is the art of having disguised the abrasive function of the detergent under the delicious image of a substance at once deep and airy [...]".

In this work, we aim at advancing the understanding of the tribological properties of these Liquid/Air interfaces and, in particular, at exploring their potential in the removal of lipids at solid surfaces in the framework of cosmetic application. Silicon wafers were used as planar test systems. They are coated with sebum and cleaning tests are carried out, using surfactant solutions as the cleaning agents. Cleaning tests are performed in presence of interfaces or in the bulk and the degree of sebum removal in each case is measured. We use silicon wafers due to the fact that their surface properties can easily be changed to mimic those of both untreated (more hydrophobic) and damaged (more hydrophilic) hair at least in terms of surface energy. Other parameters could be explored such as the roughness of the substrate. Indeed, real hairs have a particular morphology close to tiled roof. This could influence the deposition on hair and induce heterogeneities. This is nevertheless beyond the scope of this article in which we focus on the influence of the hydrophobic or hydrophilic character.

The plan of the paper is as follows. Our methods for sample preparation and the test protocols are given in Section 2. The experimental results are described in Section 3, with discussion of the effect of surface energy in Section 4 and our conclusions in Section 5.

2. Sample preparations

2.1. Hair's substrate model

Silicon wafers (5 cm diameter, Fig. 1), initially hydrophobic, were chosen as the test substrate for the detergency tests because of their very flat surface, lack of surface defects and the ease with which their surface properties could be altered. The pioneering work by Ong et al. [10] has shown the presence of two types of silanol at the silica/water interface with pK_a values 4.9 and 8.5. These are associated with surface population of 19 and 81%, respectively, leading to a small negative charge of the silicon wafers at pH = 7.

2.2. Modification of wafer's surface energy

As mentioned before, for the purpose of this study it is important to observe the cleaning efficiency as a function of the hydrophilic or hydrophobic character of the surface. In addition a good range of intermediate values of surface energies well represents the variability that is observed on the surfaces of hair fibres, from natural to weathered, or oxidatively treated hair.

The surface energy of silicon wafers was altered using a classical liquid-phase silanization [11,12]. The wafers were cleaned by rinsing first in toluene, then in chloroform in an ultrasonic bath. After these wet cleaning steps the wafers were dried in a stream of argon before being placed in a UV-ozone cleaning chamber for 25 min. After cleaning, the wafer surface was free of any impurities, the surface energy was high and the contact angle with water was very low.

The wafers were silanized immediately after cleaning by placing them in a solution of 100 μL of octadecyltrichlorosilane (OTS) in 10 mL of toluene and leaving them to soak for 5 min. After removal from the silane solution, the wafers were washed in chloroform and dried in a stream of argon before use.

The static contact angles with water for the silanized silicon wafers were measured using the TRACKER (Teclis, Lyon, France) apparatus. Twelve drops of water (~10 μL each) were placed in a cross formation on the wafer (Fig. 1a) to check that the silanization was uniform and that the contact angle was constant over the wafer surface. In general, the silicon wafers had a contact angle, θ_c, ranging 108–110° after silanization.

To obtain the range of contact angles required to mimic those of bleached and natural hair (40–100°) small intervals of UV-ozone processing were used: 30 s to 1 min of processing gave θ_c in the range 90–80°, and 3−4 min gave θ_c in the range 50–40°. Because of uncertainties in the processing, the value of θ_c was measured for every wafer post treatment. It was noted that the values of θ_c tended to drift upwards with time after UV-ozone processing – up to 10° in one week. It is suggested that this occurs because the process removes some of the silane molecules from the wafer surface leaving small gaps that can then absorb pollutant molecules from the surroundings. It was therefore necessary to clean, re-silanize and retreat the wafers before each test to ensure that the surfaces were untainted by any contamination.