Applied Surface Science 257 (2011) 9631–9638

Contents lists available at ScienceDirect

Applied Surface Science

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

New insights on contact angle/roughness dependence on high surface energy materials

S. Giljean [a,*], M. Bigerelle [b,1], K. Anselme [c], H. Haidara [c]

[a] Equipe MMPF – LPMT, EA conventionnée CNRS 4365, IUT Département GMP, Université de Haute-Alsace, 61 rue Albert Camus, 68093 Mulhouse cedex, France
[b] Laboratoire Roberval CNRS UMR 6253, Université de Technologie de Compiègne, Centre de Recherches de Royallieu, BP 20529, 60205 Compiègne cedex, France
[c] Institut de Science des Matériaux de Mulhouse (IS2M), CNRS LRC7228, Université de Haute-Alsace, 15 rue Jean Starcky, BP 2488, 68057 Mulhouse cedex, France

ARTICLE INFO

Article history:
Received 13 April 2011
Received in revised form 15 June 2011
Accepted 17 June 2011
Available online 23 June 2011

Keywords:
Wetting regimes
Roughness
Scale effects
High surface energy materials
Two liquid phase method

ABSTRACT

The relationship between wettability and roughness has been studied on micro-roughened titanium surface after different cleaning procedures. Whereas most studies addressing (super)-hydrophobic behaviors have so far dealt with the wetting of low surface energy and textured substrates in air environment, we here report on a totally novel system and configuration involving the wetting of highly hydrophilic, textured metallic materials in liquid alkane medium, the so-called two liquid phase method. Roughness characterization showed that substrates were isotropic (2D), at a lengthscale much smaller than the size of the drop, with a heterogeneous (vertical) distribution of peaks and valleys. Depending on whether the alkane that initially penetrates and resides in the pores is displaced or not by the water drop (as for air pockets in air environment), we show that different wetting regimes may appear, depending on the cleaning procedure. To our knowledge, this is the first systematic study dealing with the interplay between surface roughness, the wetting behavior and in particular the (super)-hydrophilicity of high surface energy substrates, in non water miscible liquid environments. Whenever competitive processes of liquid/liquid displacement are involved at such high surface energy and textured substrates, such as titanium implant in bone tissue, these results may contribute understanding and predicting their wetting behavior.

1. Introduction

The behavior of a drop was firstly described by Young [1] using a relationship between surface free energy of liquid/fluid (γ_{lf}), solid/liquid (γ_{sl}) and solid/fluid (γ_{sf})

$$\gamma_{sf} - \gamma_{sl} - \gamma_{lf} \cdot \cos\theta_Y = 0 \quad (1)$$

where θ_y is the Young angle. This relation is formally applicable only on surfaces that are physically smooth and chemically homogeneous. Indeed, it has been shown since that roughness and chemical heterogeneities have a critical influence on contact angle values (CA) [2–10]. This influence of roughness on CA was mainly studied on structured surfaces bearing well ordered micron-to-nanoscale patterns [11–18], with a special focus on “superhydrophilic” and “superhydrophobic” behaviors [19–24]. Numerous authors have proposed models to describe the relationship between wettability and roughness [25–29]. But most of those models and experiences, dealing in particular with superhydrophobic or superoleophobic properties, mainly involve bulk substrates or outermost surface coatings which are of low surface energy (polymers, wax, and self-assembled molecular films). On those surfaces, a partial to non-wetting behavior is observed with water (in particular), allowing easily modeling and predicting CA values on the corresponding roughened surface textures.

The Wenzel model [29] of wetting on rough surfaces uses the ratio r between the actual surface area supposed to be fully wetted by the liquid, and the projected planar area to describe the relationship between the apparent equilibrium CA measured on the rough surface (θ_W), and the Young angle (θ_Y) of the smooth surface

$$\cos(\theta_W) = r \cdot \cos(\theta_Y) \quad (2)$$

This model, which thus applies only when there is no gas entrapped beneath the drop, was extended by Cassie and Baxter [25] to involve chemical and physical surface heterogeneities, as well as gas entrapment beneath the drop. In that Cassie–Baxter

* Corresponding author. Tel.: +33 03 89 33 75 18; fax: +33 03 89 33 75 05.
E-mail addresses: sylvain.giljean@uha.fr (S. Giljean), maxence.bigerelle@utc.fr (M. Bigerelle), karine.anselme@uha.fr (K. Anselme), hamidou.haidara@uha.fr (H. Haidara).
[1] Current address: Thermique, Ecoulement, Mécanique, Matériaux, Mise en forme, PrOduction (TEMPO) EA 4542, Université de Valenciennes et du Hainaut Cambrésis, Le Mont Houy, 59313 Valenciennes cedex 9, France.

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.06.088

approach, the equilibrium CA θ_{CB} results from each wet surface fraction Φ_i, the intrinsic Young angle on which is θ_{Yi}, according to

$$\cos(\theta_{CB}) = \sum_i \Phi_i \cdot \cos(\theta_{Yi}) \quad (3)$$

The validity of the model of Cassie and Baxter (CB model) was discussed by several authors. From a physical standpoint, Oliver et al. [5] demonstrated that in several cases, CB model does not predict a correct behavior of CA on rough surfaces. At the opposite Wolansky and Marmur [30] demonstrated that CB model was well adapted for sawtooth surfaces. From a chemical viewpoint, Neumann and Good [31] showed that CB model only applies to macroscopic chemical heterogeneities. Considering only physical heterogeneities (roughness), the foundation of the CB and Wenzel models was discussed by Pease [32] and Bartell and Shepard [2,3] who showed that the CA will only depend on the roughness along the triple line, and not on the surface ratios of the heterogeneities beneath the drop. The validity of those models is still under debate [33–41]. Nevertheless, they admitted that CB model using the surface ratios can be applied to homogeneous rough surfaces if the characteristic size of the roughness is small enough against drop size. In our study, the size of the drop compared to the size of the isotropic roughness allows validating both models, and to either consider the triple line or the surface ratio beneath the drop to account for the CA/roughness dependence.

As stated above, the wetting mechanisms on rough (topographically structured) substrates have been essentially discussed and modeled on materials with low surface energy. On the contrary, the wetting behavior of rough substrates of high surface energy materials still remains sparsely investigated and thus misunderstood. Lim et al. [42,43] studied the influence of roughness on CA of titanium surfaces, although this roughness was quantified by the unique R_a value of the arithmetic average of the absolute vertical deviations, ignoring the many other and often more significant roughness parameters. In the biomedical field, a lot of studies have dealt with the understanding of the mechanisms of cell response to roughness of implants [44–47]. Similarly, the wettability of implants is known to be a crucial application parameter and information [48–51]. The wettability of those implants strongly depends on the surface cleaning [52–54] or surface chemical treatment [55]. However, this influence of the cleaning process is not systematically assessed and optimized when measuring CA on these implants in clinical applications, contrary to laboratory experiments where such surface cleaning and assessment (CA, spectroscopy) of samples is common and recurrent. Furthermore, for metal implants that undergo multiple-step treatments and manipulation (roughening, sterilization, packaging), some of which introduce organic contaminations, not only the wettability (CA) is impacted by the surface state and/or cleaning procedure, but also the often desired penetration and anchoring of biological materials into the surface roughness. Most of CA measurements in the biomedical field are made in air environment on metallic implants with different roughness, and using water as the test liquid. These air-contaminated and often *poorly* cleaned metallic surfaces essentially display a low surface energy, as attested by the finite water CAs which are usually measured under those conditions. A particularly interesting exception to that common practice has been proposed by Rupp et al. [56], with the objective to enhance the surface free energy and the hydrophilicity of sandblasted titanium implants. In their approach, these authors developed a procedure in which the implants were produced under N_2 protection and stored in an isotonic NaCl solution to preserve the previously performed chemical surface activation, until implant placement. The in vivo results have effectively confirmed their higher osteointegration and a decrease of the healing time in clinical applications [57,58], highlighting the cleaning and preservation conditions on in vivo surface activity of metal implants.

Our objective in this paper was to study the relationship between wettability and roughness on high surface energy metallic implants, presenting a wide range of micro-scale roughness. The roughness was produced by a single full step process that eliminates chemical differences between samples, and generates, at a lengthscale much smaller than the size of the drop, isotropic surface (2D) roughness characterized by a heterogeneous (vertical) distribution of peaks and valleys, at the difference of the patterned surfaces used in most of similar studies [11–16]. Since surface contamination, even at the scale of a monolayer, can drastically modulate the influence of roughness on wetting, especially on high surface energy substrates (metallic implants), the influence of these cleaning effects was systematically assessed and taken into account. As cleaned metallic implants are high surface energy materials, a total spreading is expected and observed in air environment for an efficient surface cleaning procedure and further preservation from contamination. As a consequence, CA measurements were performed using the “two liquid phase” method [59]. In that configuration, spreading of the drop is reduced by the presence of a surrounding non miscible liquid, which creates a lower interface energy γ_{sl^*} at (solid/surrounding liquid) interface, compared to the reference surface energy γ_{sl} in air. A discussion on the structure of the rough interface involving the drop, the metallic substrates and surrounding liquid is finally proposed for the different cleaning methods, to account for the observed CA values and wetting behaviors (regimes). Besides the above practical (biomedical) aspects, we show that under well defined criteria (derivable statistically), the usual and basic roughness parameter R_a can be relevant, in place of the formal surface ratios, for discussing the wetting behavior of an ensemble of rough surfaces which display self-similar topographical features. On such an ensemble of surface textures, our results show that this is the case, provided that the R_a parameters are shown to scale linearly with the essential topographical lengthscales of the rough surfaces, and thus with the surface ratios as we show it in the following.

2. Experimental

2.1. Materials and surface preparation

A 5 mm thick plate of pure Titanium grade 1 (ACNIS International) was used in this study. On that Plate 22 areas were electro-eroded using Electrical Discharge Machining on a spark erosion machine (Charmilles S.A) with adjustable parameters (power, electrode diameter) which allow realizing samples covering a wide range of roughness parameters. Then the plate was cut in order to obtain 22 samples of diameter 20 mm, with 22 gradually increasing roughness levels. To illustrate this roughness level, the amplitude roughness parameter R_a ranges from 1.1 μm to 20 μm for roughness level going from 1 to 22. Mirror polished titanium samples with R_a = 0.01 μm were also used as flat reference surface. The polishing has been carried out on a Pedemax 2 automatic polishing machine provided by Struers. Silicon carbide papers from grade 80 to grade 4000 were successively used.

2.2. Sample cleaning

Three different cleaning methods were used in this study in order to evaluate the influence of surface cleaning on the relationship between wettability and roughness. Firstly, a water rinsing followed by nitrogen drying was called “type 0” cleaning. “Type I” cleaning was defined as successive soakings in ultrasonic baths of acetone, cyclohexane and acetone, followed by water rinsing and