



New strategies to create technologically relevant superomniphobic coatings on sol-gel base



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ABSTRACT

Omniphobic and superomniphobic sol-gel coatings have been prepared on technical scale by sol-gel formulations modified with a perfluoropolyether and/or a fluoropolymer nanoparticle dispersion. Single and two-layer coatings were prepared by spraying or coating with a doctor blade. They exhibited a broad range of different morphologies leading to different wetting behavior. Under certain preparation conditions (spraying at elevated temperature, high surface coverage), the single-layer coatings with perfluoropolyether and fluoropolymer nanoparticles exhibited a hierarchical structuring at various length scales, high roughness and aspect ratio, re-entrant structures and superomniphobic behavior. The mechanical stability of these layers was sufficient to maintain superhydrophobicity and oleophobicity after a harsh wet abrasion test. Two-layer coatings with a smooth low-energy top coat on a rough fluorine-free base coat had a higher mechanical stability but showed an unsatisfactory wetting behavior. Systematic investigation of the correlations between roughness, liquid surface tension and advancing/receding contact angle of water, water-ethanol mixtures and hexadecane confirmed the existing theories. The self-cleaning properties of the rough coatings were good for polar soils; for oils they are very sensitive to layer defects.

1. Introduction

Easy-to-clean or self-cleaning surfaces are in the focus of interest for a broad variety of applications as e.g. facades, windows, solar cell panels, food containers, kitchen equipment, or oil tubings. Superhydrophobic coatings repelling water-based or water-soluble soil as well as particles in contact with water are now state of the art [1,2]. The self-cleaning of surfaces from oily and greasy soils with low surface tension remains, however, a great challenge. This application requires superhydrophobic and superoleophobic (“superomniphobic”) properties, i.e. coatings that exhibit high advancing contact angles and a low contact angle hysteresis for all liquids independently of their surface tension.

In 1977 Barthlott and Ehler [3] discovered that the self-cleaning behavior of lotus leaves results from an interplay of chemistry (low surface free energy) and roughness. The influence of the surface roughness on the wetting behavior was, however, studied much earlier [4,5].

Surfaces with a negligible or low roughness are usually wetted in the homogeneous or Wenzel regime: the surface is covered completely,

all voids are filled by the liquid. The advancing contact angle is increased by roughness but the contact angle hysteresis is high. The measurable macroscopic or apparent contact angle θ_{app} is determined by the Wenzel equation [4]

$$\cos \theta_{app} = r_w \cos \theta_{in} \quad (1)$$

θ_{in} is the intrinsic contact angle, the thermodynamic contact angle of a perfectly smooth and homogeneous surface. The Wenzel roughness r_w is the ratio between the true area of the rough surface and the area projected on the xy plane. Wenzel's concept does, however, not consider the contact angle hysteresis.

Beyond a certain threshold value of the Wenzel roughness the wetting of low-energy surfaces with intrinsic contact angles $> 90^\circ$ is described by the heterogeneous or Cassie-Baxter regime: Due to roughness-induced energy barriers the liquid cannot enter the voids between the asperities; only a part of the surface area is wetted and air is entrapped. The apparent contact angle θ_{app} is high with a low or even negligible hysteresis, i.e. both θ_{adv} and θ_{rec} are close to θ_{app} . In the Cassie-Baxter regime θ_{app} is predicted by the Cassie equation [5]:

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$$\cos \theta_{app} = f_1 \cos \theta_{in} - f_2 \quad (2)$$

where f_1 is the solid surface fraction wetted by the liquid and f_2 is the interface fraction between the liquid and entrapped air with $f_1 + f_2 = 1$ [6]. Although it is often difficult to determine or estimate f_1 and f_2 , it can be concluded from Eq. (2) that high apparent contact angles are reached if f_1 is small compared to f_2 . Low wetted areas f_1 and high water contact angles can be obtained by hierarchical or fractal structures with a roughness on several length scales [7,8]. For a comprehensive description of the wetting of hierarchical surfaces, all roughness levels larger than the hydrodynamic diameter of the liquid molecules [9] and smaller than the size of the liquid drop [10] have to be taken into account, leading to more complicated wetting regimes (e.g. Wenzel-in-Wenzel, Cassie-in-Wenzel, Wenzel-in-Cassie, Cassie-in-Cassie for two roughness levels) [11].

The wetting of rough surfaces with high aspect ratio of the surface asperities is often determined by metastable states similar to the Cassie-Baxter regime where the slope of the side walls prevents the liquid from entering the voids [12]. Numerical calculations for randomly structured surfaces by David and Neumann [13,14] yielded a series of wetting minima; advancing and receding contact angles are the highest and lowest possible contact angles corresponding to the outer minima.

High intrinsic contact angles are observed on materials with a very low surface energy, obtained e.g. by fluorine chemistry. Very interesting examples are the so-called POSS [15] or ORMOSILs [16], polyhedral oligomeric silsesquioxanes with fluorinated side chains. In the last years, a new class of mechanically stable organic-inorganic superhydrophobic coatings was created by sol-gel formulations including fluorine compounds as fluorinated polyethers and organosilanes with fluorinated side chains [17]. Sol-gel coatings combine the specific advantages of organic and inorganic coatings. Their properties (e.g. charge or wettability) can be modified in a wide range by functional groups, additives and fillers opening perspectives for widespread application as e.g. primers, scratch-resistant and barrier coatings or antiadhesive, “easy-to-clean” and anti-fingerprint varnishes [18,19]. Smooth and homogeneous spin-coated sol-gel layers including perfluoropolyether with alkoxy silane functionalities exhibited low surface tensions of 14–16 mN/m and static contact angles of 104°–109° and 64–68° for water and hexadecane, respectively [20,21]. Dynamic contact angle measurements gave a low contact angle hysteresis of about 10° for water [22].

To obtain superhydrophobic behavior, it is necessary to combine low surface energy with increased surface roughness [1–3]. Numerous examples of superhydrophobic surfaces with hierarchical structures are described in the literature, created e.g. by anodical oxidation and roughening of aluminum [23], or hairy structures [24]. On larger scale, such surfaces were produced by assembly of hydrophobically functionalized micro- and nanoparticles [7,8,25–28] and by sol-gel technique [29–32]. Taurino et al. [33] combined a sol-gel formulation with perfluoropolyethers and metal alkoxide precursors. The resulting air-brushed coatings reached a mean square roughness up to 3 μm, hysteresis-free water contact angles of about 150° and in some cases even contact angles of the unpolar liquid hexadecane above 100° with low hysteresis. A higher scratch resistance was obtained by sprayed sol-gel multilayer assemblies with a fluoropolymer on top [34]. Li et al. created superhydrophobic fluorinated silica sol-gel layers by dip-coating and calcination [35]. Other authors incorporated silica micro- and nanoparticles in the fluorinated layers [36–38].

To obtain superomniphobic properties, i.e. high contact angles and low hysteresis of all liquids including unpolar liquids with low surface tension, it is not sufficient to have a low surface energy and a hierarchical structure. If the intrinsic contact angle of the liquid is < 90°, the liquid usually penetrates all voids, surfaces are wetted in Wenzel regime. Increasing roughness leads to a reduction of the apparent contact angle. Nevertheless Cassie-like states with high advancing and receding contact angles may dominate if the solid

surface features so-called re-entrant structures with negative slopes of the structure sidewalls [15,39,40]. These structures form energy barriers that prevent the liquid from entering the voids. A very effective omniphobic morphology was derived from the skin of small insects, the springtails [39]. It consists of mushroom-like, T- or serif-T-shaped structures with sharp edges and undercuts.

Superomniphobic surfaces thus have to fulfil three conditions: a low surface energy, a hierarchical structure, and re-entrant geometries (undercuts). Such surfaces have been prepared successfully on laboratory scale e.g. by anodical oxidation of aluminum [41], electrospinning, etching [15], spraying [42], silicon micromachining [43], reverse imprint lithography [44], etching metal meshes [45] or by using colloidal particle templates to create reverse particle structures [46]. Also with some rough fluorinated sol-gel layers high contact angles of hexadecane were reached [33].

In the present study, mechanically stable, technically relevant superhydrophobic and oleophobic coatings were developed by a novel combination of sol-gel chemistry with a perfluoropolyether and a fluoropolymer nanoparticle dispersion. Under certain conditions they formed superomniphobic layers with a hierarchical roughness and re-entrant geometries. By variation of the coating procedure and technological parameters, coatings with different roughness, aspect ratio and micro-/nanostructure are produced. With these layers, the influence of technological parameters as well as correlations between surface morphology and roughness, wetting behavior and mechanical stability was studied systematically. Structure-property relationships were derived on the basis of existing theories and models.

2. Materials and methods

2.1. Materials

The sol-gel coatings H 1006 and H 5055 are commercial products by FEW Chemicals (Wolfen, Germany). Some details of the composition and the sol-gel chemistry are given in refs. [17,18]. The perfluoropolyether Fluorolink® S10 was purchased by Solvay Specialty Polymers Italy S.p.A., the fluoropolymer dispersion 3MTM Dyneon™ Fluoroplastic FEP 6300GZ by Dyneon GmbH. SiC particles UF-05 and UF-25 were obtained from H. C. Stark GmbH, SiO₂ nanoparticles Levasil® 100/45 from Akzo Nobel Pulp and Performance Chemicals AB, and ultra-high molecular weight polyethylene GUR® 2126 from Ticona GmbH.

The following liquids were used for contact angle measurements, wet abrasion and cleanability tests:

- ultrapure water (Purelab Plus, ELGA Lab Water; conductivity 0.055 μS/cm), surface tension 72.6 mN/m
- ethanol absolute (VWR Chemicals, France), surface tension 21.7 mN/m
- n-hexadecane (Reagent Plus 99%, Sigma-Aldrich), surface tension 26.4 mN/m
- honey (NektarQuell Blütentracht, Ullis Honigmarkt, München, Germany)
- sunflower oil (Thomy Reines Sonnenblumenöl, Nestlé, Germany)
- silicone oil Korasilon 10.000 (Obermeier GmbH, Bad Berleburg, Germany)
- 2,5 g/l sodium dodecylbenzenesulfonate (techn. 80–85%, Fluka, Switzerland) in ultrapure water
- n-hexane (p.a. 99%, Merck KGaA, Germany)
- Eurostar 65 (DC Druckchemie GmbH, Germany)

2.2. Preparation of sol-gel layers

For the single-layer coatings, mixtures of acid-catalyzed hydrolysis and condensation products of different functionalized silanes basing on the formulations H 1006 or H 5055 were blended with the fluoropolymer dispersion FEP 6300GZ and Fluorolink® S10. The dispersions

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