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Influence of dodecanol on wetting behavior of superhydrophobic surfaces

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Abstract: Digital processing of the optical image of a sessile droplet was used to study the influence of dodecanol vapors and condensate on the wettability of superhydrophobic coatings by water. Two types of coatings with very different morphologies were used to estimate the stability of the superhydrophobic state in the presence of dodecanol at different regimes of interaction of tested superhydrophobic coatings with dodecanol vapors, including preliminary condensation of dodecanol inside the substrate pores/grooves at different temperatures, a short-term contact of dodecanol vapor with the superhydrophobic coating with the preliminary deposited water droplets and, finally, a long-term contact between substrate with deposited water droplets and the vapor phase saturated with dodecanol vapor. The set of experimental data indicate only minor variations of water contact and roll-off angles for all regimes studied. Such wettability behavior evidences good persistence of superhydrophobic state in conditions of contact with long-chain alcohol vapors.

Keywords: surface modification, laser treatment, anodic etching, superhydrophobicity, wettability, nanostructured surfaces

1. Introduction

Recent advances in the control of surface wetting lead to the development of a diversity of functional materials with the special wettability for the industrial applications. Superhydrophobic surfaces have attracted the intense interest of researchers due to their importance in both academic research and practical applications. One of the key points for academic studies is the behavior of superhydrophobic surfaces in contact with surfactant presented either in aqueous phase, in air phase or on the solid surface. Until now the main attention in the literature was paid to the influence of surfactants dissolved in aqueous phase on the wettability of superhydrophobic surfaces (Mohammadi et al., 2004; Ferrari et al., 2006; Chang et al., 2007; Krasowska et al., 2009; Ferrari and Ravera, 2010; Krasowska et al., 2011; Milne et al., 2011; Wahlander et al., 2015; Martin et al., 2017), and the role of surfactants in that case has been studied experimentally in detail. Since many of superhydrophobic coatings are aimed to be exploited in outdoor conditions and in close proximity to large cities where the atmosphere is contaminated with various surfactants, the problem of preservation of superhydrophobic state in the presence of organic airborne contaminants is of great importance. The evolution of wettability of superhydrophobic surfaces by aqueous phases will be significantly affected by the surface free energy of organic contaminants present in the atmosphere, their solubility in water, vapor pressure, their chemical structure and the morphology of textured surface. During the exploitation of the superhydrophobic coatings in outdoor conditions, where the organic airborne contaminations are ubiquitously present, the surfactants initially adsorb from the vapor phase onto a superhydrophobic surface or simultaneously adsorb on superhydrophobic surface/air and aqueous droplets/air interfaces. Typically organic airborne contaminations act as surfactants for aqueous medium/air and aqueous medium/solid interfaces. At the same time, for the superhydrophobic

coatings fabricated on the basis of fluorine-containing hydrophobic agents such contaminations, being surface inactive with respect to the superhydrophobic coating/air interface, do not form compact monolayer atop of textured layer, but, at relatively high vapor pressures, condense inside the nanogrooves of the superhydrophobic surface. In the literature, the effect of surfactants, either absorbed by the solid substrate or presented in the vapor phase, on the wettability of superhydrophobic substrates by water was not considered so far.

Saturated alcohols as surfactants for water-air interface were intensively studied in the literature (Vollhardt and Emrich, 2000; Vollhardt et al., 2000; Jachimska et al., 2001; Krzan and Malysa, 2002). Atmospheric urban pollutions in vicinity of large industrial cities of Europe, China, India, etc. contain aerosols enriched with medium chain and long-chain alkanes, alcohols and fatty acids. These organics are emitted directly into the atmosphere as fine or coarse aerosol particles by plenty of sources including power stations, chemical industry products, meat cooking operations, interaction of a carbon oxide and hydrogen with fatty hydrocarbons, with biomass converting, etc. (Oliveira et al., 2007; Fu et al., 2008; Li et al., 2014; Carrion-Fite, 2016; Ren et al., 2016). In particular, dodecanol is a component of diversified industrial processes, such as manufacture of surfactants, detergents, pharmaceuticals, lubricating oils, flavoring agents, and a major component for numerous paints and coatings.

In this paper, we will analyze wettability of superhydrophobic surfaces, exposed to dodecanol vapors according to different procedures. We will use the dodecanol, as a representative of saturated alcohols with low vapor pressure. The simultaneous measurement of the variation in surface tension of water droplets in the presence of dodecanol will be used to estimate the kinetics of redistribution of dodecanol between different parts of the system under study at various routes of dodecanol delivery. We will show that the heterogeneous wetting regime with high contact angle and low fraction of the wetted area is preserved in all considered conditions. Besides, the initial stages of contact of a water droplet with dodecanol molecules are accompanied by an abrupt decrease in surface tension and an increase in contact angle. The analysis of the parameters of the three-phase contact for the considered systems, such as fraction of wetted area f and the product of wetting tension on surface roughness, on the basis of the approach developed in our recent studies (Boinovich and Emelyanenko, 2012), allows better understanding of the outdoor operation of superhydrophobic coatings.

2. Material and experimental methods

We used two types of aluminum alloy substrates: the AMG2 aluminum-magnesium alloy with around 2 wt.% of Mg, and AD0 alloy containing 99,5% of Al, with Fe and Si as the main impurities. To prepare the superhydrophobic samples, the sheets of both types of alloys were cut into pieces with a size of $15 \times 15 \times 1$ mm³. Preliminary treatment of the plates included degreasing in potassium hydroxide solution and rinsing with distilled water. Then the AMG2 substrates were textured using pulsed nanosecond IR laser treatment. For that, the Ytterbium Fiber Laser with wavelength 1.064 μ m and effective power 20 W was used, as described in (Emelyanenko et al., 2015). The samples were raster scanned at a linear speed of 50 mm/s with parallel line pitch of 0.02 mm, a pulse duration of 50 ns, the repetition rate of 20 kHz and peak power of 0.95 mJ in TEM₀₀ mode. The texturing of AD0 substrates was based on anodic oxidation in the galvanostatic regime in a 20 vol.% phosphoric acid solution, followed by washing with distilled water. To increase the surface density of chemisorption-active sites, both types of the textured substrates were subjected to ozone treatment in a UV.PC.220 ozonator (Bioforce Nanosciences) under UV irradiation with the intensity of 14 mW/cm² for 60 min. After UV-ozone treatment, the sample was exposed to the vapors of methoxy- $\{3-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8\text{-pentadecafluorooctyl)-oxy]-propyl\}$ -silane at 95 °C, leading to the chemisorption of the hydrophobic molecules onto the textured surface (Emelyanenko et al., 2015). Subsequent thermal treatment at temperatures of 120-140 °C in the presence of water vapor resulted in the formation of a cross-linked surface monolayer of fluorooxysilane, which provided both the low surface energy of the substrate and the stable superhydrophobic state.

The morphology of the coating was studied using a Carl Zeiss Supra 40 VP scanning electron microscope at 5 kV acceleration voltage using secondary (InLens, SE2) electron detectors. Deionized water was used as the testing liquid for characterizing wettability of the superhydrophobic coatings

and for studying the effect of dodecanol molecules presented in the vapor phase or inside the pores of superhydrophobic substrates on the evolution of the parameters of an individual water droplet deposited on the superhydrophobic surface. Chromatography grade n-dodecanol (>99.5%) was purchased from Acros and used as received.

The main goal of this study was to estimate an impact of environmental organic pollutions on the functional performance of the superhydrophobic coatings. To model the different conditions from the casual emission of pollutants of different duration, intensity and atmospheric conditions, leading to various degree of contaminations concentration in the atmosphere we have used four types of experiments modeling different regimes of airborne surfactants impact on both types of fabricated superhydrophobic substrates.

In the first type of the experiment, the superhydrophobic substrate was exposed to saturated dodecanol vapor inside the sealed vessel at $T=25\text{ }^{\circ}\text{C}$ for 1 h. Since the surface tension of fluorooxysilane is less than the surface tension of dodecanol (Krafft and Riess, 2009), the exposure of the superhydrophobic substrate to saturated dodecanol vapors leads to dodecanol condensation inside the grooves of textured substrate. At the same time, the convex tops of surface texture remain free of adsorbed dodecanol molecules. After that the superhydrophobic substrate was transferred inside an experimental cell, a droplet of deionized water was placed onto the superhydrophobic surface and the experimental cell was kept in the conditions of 100% water vapor humidity (Boinovich et al., 2010). In this type of experiment, we studied the effect of dodecanol vapor accumulated inside the grooves/pores of a superhydrophobic substrate on the parameters of an individual water droplet deposited on the superhydrophobic surface. The cell was kept at room temperature of $25\text{ }^{\circ}\text{C}$ and water droplet contact angle and surface tension were monitored during 24 h.

In the second type of the experiment the superhydrophobic substrate was exposed to saturated dodecanol vapor at $T=30\text{ }^{\circ}\text{C}$ for 30 min inside the sealed vessel, then the sample was transferred into an experimental cell and the 24 h evolution of water droplet parameters for the droplet deposited onto the substrate with capillary condensed dodecanol was studied at $T=25\text{ }^{\circ}\text{C}$. In this type of experiment, the character of interaction between the dodecanol and the water droplet is the same, as in the experiment of the first type. However, due to higher temperature and larger dodecanol diffusion coefficient, more dodecanol was accumulated inside the grooves/pores of a superhydrophobic substrate.

In the third type of the experiment, a bowl with dodecanol was placed inside the experimental cell with the sessile water droplet on the superhydrophobic substrate for 1 h and then removed from the cell. Finally, in the experiment of the fourth type the bowl with dodecanol was kept in the experimental cell during the whole duration (24 h) of the experiment at $T=25\text{ }^{\circ}\text{C}$.

The choice of testing regimes was dictated by the following factors. On the one hand, the kinetics of pore filling is affected by the temperature through the diffusion coefficient. To provide higher degree of pores filling with the capillary condensed dodecanol at lower exposure time, the increased temperature of sample exposure to dodecanol vapors is required. On the other hand, placing the source of dodecanol inside the experimental system with the water droplet already deposited on the substrate (types 3 and 4 of the experiment), we simultaneously enrich the vapor phase with dodecanol vapors and condense dodecanol into substrate pores. Besides, the dodecanol is adsorbed on droplet surface. In the conditions of limited time of the dodecanol source presence in the experimental system (type 3) the equilibrium distribution of dodecanol in the experimental system was not reached. In contrast, at constant presence of the dodecanol source (type 4), the stationary state is achieved in approximately 15-20 h.

The variation in experimental conditions allows reproducing the ambient conditions of superhydrophobic surfaces contamination with the different concentration of surfactants and various conditions of their presence in the atmosphere.

In all types of experiment, optical images of the water droplet in the process of its temporal evolution were stored on a computer disk and then analyzed using digital image processing and the Laplace fit optimization procedure. This analysis makes possible to determine the evolution of different parameters of a sessile droplet, including contact angle, surface tension, volume and surface area of the water droplet (Emelyanenko and Boinovich, 2001). The initial contact and roll-off angles

were measured at five different points on the superhydrophobic sample surface in separate experiments to characterize the wettability of the whole sample.

3. Method for the determination of the wetting tension and the wetted area fraction for a superhydrophobic substrate

It was shown in our recent studies that for rough materials the additional information about the parameters of three-phase contact is available from the analysis of the temporal evolution of the droplet shape parameters. In the heterogeneous wetting regime, the liquid droplet partially contacts the solid surface and partially the air interlayers trapped within grooves and cavities on the surface. In this regime, the apparent contact angle formed between the sessile droplet and the substrate is determined by the parameters of three-phase contact according to the Cassie-Baxter equation (Cassie and Baxter, 1944), which, taking into account the Young equation, can be written as follows:

$$\cos\theta_{CB} = r_w f \frac{(\sigma_{SV} - \sigma_{SL})}{\sigma_{LV}} + (f - 1), \quad (1)$$

where θ_{CB} is apparent (Cassie-Baxter) value of the contact angle, r_w is the roughness coefficient for the wetted area (part of solid surface being actually in contact with the liquid droplet), f is the fraction of wetted area (the ratio of the projection of wetted area on the apparent plane of the droplet base, to the area of the droplet base), σ_{SV} , σ_{SL} and σ_{LV} are solid-vapor, solid-liquid and liquid-vapor free surface energies, respectively.

At the prolonged contact of the liquid droplet with the substrate, the wetting tension, equal to the difference between solid/vapor and solid/liquid free interfacial energies ($\sigma_{SV} - \sigma_{SL}$), in general, varies with time. The experimental data obtained upon the evolution of contact angle and droplet surface tension at the long-term contact between the droplet and the substrate can be plotted as $\cos\theta_{CB}$ versus $1/\sigma_{LV}$. The dependence $\cos\theta_{CB} = f(1/\sigma_{LV})$ exhibits a complex behavior. However, within certain time intervals, when the fraction of wetted area f , roughness r_w and wetting tension retain approximately constant values at the variation of surface tension σ_{LV} and effective contact angle θ_{CB} , this dependence may be well approximated by a straight line. The slope of this line at the considered time intervals characterizes the value of the product $r_w(\sigma_{SV} - \sigma_{SL})$, and the intercept is equal to $(f-1)$. Thus, plotting the dependence $\cos\theta_{CB} = f(1/\sigma_{LV})$ and selecting the linear sections, for which the straight line fit intercepts the ordinate axis between 0 and -1, one can determine both the fraction of wetted area and the value of $r_w(\sigma_{SV} - \sigma_{SL})$. The sign of the latter parameter provides information on the real state (hydrophobic versus hydrophilic) of that local part of the substrate which is contacting the liquid meniscus (Boinovich and Emelyanenko, 2012). This method allows obtaining reliable results when the variation of $\cos\theta_{CB}$ and $1/\sigma_{LV}$ with time is much larger than the experimental scatter in above parameters.

4. Results and discussion

The details of the surface morphology of samples textured by both anodic oxidation and nanosecond laser treatment are shown in Fig. 1. These SEM images show that the multimodal roughness was obtained after both types of texturing treatment. The advancing contact angles and roll-off angles measured for the studied samples are given in Table 1.

Table 1. Initial wettability parameters of studied superhydrophobic samples

Parameters	Superhydrophobic sample textured by laser treatment	Superhydrophobic sample textured by anodic oxidation
Advancing contact angle, deg.	170.8±0.7	171.6±1.0
Roll-off angle, deg.	1.3±0.3	1.2±0.2

High advancing contact angles and low roll-off angles indicate the superhydrophobic state of both samples, while a low scattering of both contact and roll-off angles for studied samples evidence uniform wettability of their surface.

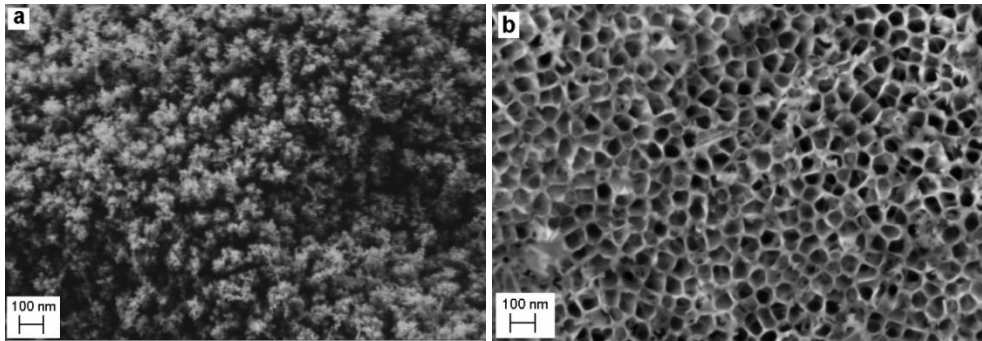


Fig. 1. The details of the surface morphology for a superhydrophobic AMG2 alloy, textured by nanosecond laser treatment (a) and for an AD0 substrate, textured by anodic oxidation (b)

The experimental data on the evolution of the contact angle and the surface tension of water droplet versus time of contact between the droplet and the superhydrophobic substrate textured by anodic treatment is presented in Fig. 2. Each graph for the temporal evolution of both the contact angle (Fig. 2a) and the surface tension (Fig. 2b) shows the behavior of parameters during above-described four types of experiment.

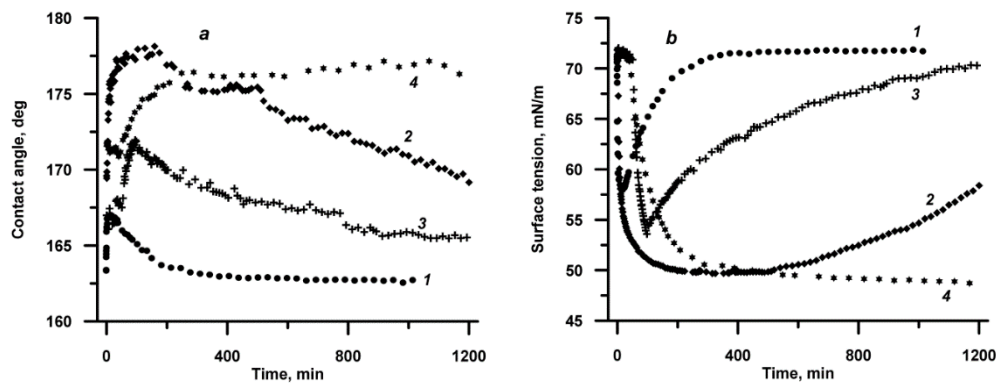


Fig. 2. Evolution in time of the contact angle (a) and the surface tension (b) of the aqueous droplet placed on the surface of the superhydrophobic AD0 aluminum substrate textured by anodic oxidation, in four different modes of presence of dodecanol in the system: (1) the substrate was exposed to dodecanol vapors at 25 °C for 1 h; (2) the substrate was exposed to dodecanol vapors at 30 °C for 30 min; (3) the source of dodecanol vapors (the bowl with liquid dodecanol) was placed for 1 h inside the experimental cell with the substrate and sessile aqueous droplet and then taken off the cell; (4) the source of dodecanol vapors was present inside the experimental cell for the whole duration of the experiment. For all modes, the evolution of the contact angle and the surface tension was studied at 25 °C

The behavior of contact angle is similar in different experiments. Namely, at initial stage of contact between the droplet and substrate having a duration from a few seconds to several minutes, the transfer of dodecanol onto droplet/vapor interface either from the pores in the substrate (experiments of first and second type) or from the vapor phase (experiments of third and fourth type) result in sharp decrease in droplet surface tension. It is worthy to note that the formation of an adsorbed monolayer of dodecanol at the solid/vapor interface is highly unlikely. If this adsorption took place, the result would be an increase in the substrate surface free energy, because the surface free energy of fluorinated chains of fluoroxyasilane is less than that of hydrocarbons (Boinovich and Emelyanenko, 2008; Krafft and Riess, 2009). However, since the superhydrophobic substrates used in this study are wetted with dodecanol, a capillary condensation of dodecanol into the pores of the substrate becomes possible at sufficiently large alcohol vapor pressure. At the same time, since the monolayer adsorption on top of convex ridges between the grooves remains energetically unfavorable, one can consider the solid/air surface tension unaltered as long as the grooves/pores are not completely filled by dodecanol and the heterogeneous wetting regime dominates.

Now let us consider, what happens with solid/liquid interfacial energy if the dodecanol may attain this interface either from vapor or from the filled pores of the substrate. According to Reh binder's rule of polarity matching, the molecule can be considered as surface active if its deposition on the surface leads to a decrease in the interfacial jump of polarity (Reh binder, 1978). Thus, following to above definition, the dodecanol molecule can be considered as a surface active with respect to the superhydrophobic substrate/water interface, because the orientation of a polar group of adsorbed alcohol molecule inward the water phase and of its hydrocarbon tail towards substrate will decrease the jump of polarity. Hence, the adsorption of dodecanol at that interface is energetically favorable. At the same time, such adsorption is kinetically limited by either dodecanol dissolution in water from the vapor phase or by diffusion along the solid/air interface within incompletely filled pores. Due to such kinetic limitations in the first stage of contact between the droplet and substrate in the presence of dodecanol the solid/liquid interfacial energy remains unaffected.

Therefore, according to the Young equation, the local contact angle which is equal to the Young angle for the considered system, tends to increase upon a sharp decrease in droplet surface tension. Consequently, the apparent contact angle has to increase as well. Indeed, the behavior of the contact angle for all types of experiment agrees well with the presented analysis. However, the behavior of the droplet surface tension at long times of contact is notably affected by the type of experiment. Since for all types of experiment, except the last one, when the source of dodecanol is continuously present in the experimental cell, the amount of dodecanol captured by the substrate (type 1 and type 2) or captured by the substrate, the droplet surface and distributed in vapor phase (type 3) is limited, the redistribution of the alcohol along the whole system upon long-term experiment results in droplet surface tension increase. Besides, since the experimental cell is not hermetically sealed, some fraction of dodecanol escapes from the cell by evaporation. That is why in the experiments where the dodecanol was delivered to the substrate or to the experimental cell at $T=25\text{ }^{\circ}\text{C}$ when its vapor pressure is low (types 1 and 3), the amount of alcohol on droplet/air interface after several hours of the experiment turns out to be small. The latter fact is proved by the value of droplet surface tension, which tends to value characteristic of pure water (Fig. 2b). In contrast, in the experiment where the dodecanol condensation inside the pores was performed at $T=30\text{ }^{\circ}\text{C}$ (type 2) when the alcohol vapor pressure is essentially higher, the amount of dodecanol captured by the substrate appears to be notably higher. This leads to the transition of dodecanol from the pores to solid/water interface and its adsorption, causing a decrease in σ_{SL} and, according to the Young equation, a minor decrease in both Young and apparent contact angles. Finally, the behavior of both the surface tension and the contact angle for the experiment in which the source of dodecanol vapors was continuously present in the experimental system (type 4) indicates that although some decrease in σ_{SL} takes place, the dominating process is the decrease in the droplet surface tension. Nevertheless, for all types of experimental conditions, the contact angle remains essentially higher than 150° .

To better understand the processes that take place during dodecanol adsorption at the substrate/water interface, we analyzed the data obtained on the evolution of the surface tension and the contact angle, using the approach described above. For that, the experimental data presented in Fig. 2 were replotted as $\cos\theta$ versus $1/\sigma_{LV}$. Here we will demonstrate the applicability of described method on the basis of experimental data obtained in the experiment of type 2 for the superhydrophobic substrate textured by anodic oxidation. In Fig. 3. the experimental data is presented in the corresponding coordinates for a superhydrophobic substrate exposed to dodecanol vapor at $T=30\text{ }^{\circ}\text{C}$ for 30 min prior to water droplet deposition onto the substrate.

The presence of three sections characterized by the linear dependence of $\cos\theta$ versus $1/\sigma_{LV}$ makes it possible to trace the variation in characteristic features of contact between the aqueous droplet and the superhydrophobic substrate. For time segments of droplet parameter evolution during which the variation of droplet surface tension is accompanied by neither alteration in the portion of the wetted area below the droplet, f , nor variation of wetting tension, the cosine of the contact angle is linearly dependent on the inverse surface tension of the droplet. A change in either of the above parameters, f or $r_w(\sigma_{SV} - \sigma_{SL})$, is revealed as a transition from one linear segment of the analyzed dependence to another.

From the slopes and intercepts for each of the linear sections in Figure 3, we have determined the fractions of wetted area underneath the droplet, f , and the product of the roughness coefficient for the wetted area on wetting tension $r_w (\sigma_{SV} - \sigma_{SL})$, for the corresponding time intervals of contact between the droplet and the substrate. These data, together with similarly determined values for all types of experiments and for both samples studied in this work, are summarized in Table 2. Note that for the experimental conditions of type 4 (at constant presence of dodecanol source in the experimental cell) only two sections characterized by the linear dependence of $\cos\theta$ versus $1/\sigma_{LV}$ were detected for both types of substrates.

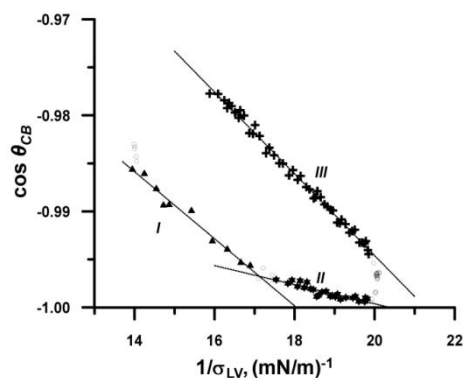


Fig. 3. Analysis of wettability evolution on the basis of Eq. (1) for an aqueous droplet on the superhydrophobic AD0 aluminum substrate textured by anodic oxidation. Prior to the droplet deposition, the substrate was exposed to dodecanol vapors at 30 °C for 30 min (experimental conditions of type 2). Symbols are experimental points, different symbols were used for points, assigned to different sections showing linear behavior; the lines show corresponding linear fits; open circles used for transient points between linear sections

The negative sign of $r_w (\sigma_{SV} - \sigma_{SL})$ indicates that for the droplet with adsorbed dodecanol, the Young contact angle is greater than 90°. Because of intensive adsorption of dodecanol at the water/air interface and a corresponding steep decrease in surface tension, the fraction of the wetted area starts to decrease, but then begins to increase as a result of dodecanol adsorption to the droplet/substrate interface. The latter process leads to a decrease in interfacial energy in the contact zone between water and the substrate, and the wetting tension ($\sigma_{SV} - \sigma_{SL}$) becomes less negative. However, we note that a decrease in the fraction of the wetted area may also cause a decrease in roughness coefficient r_w for the texture of pores perpendicular to the surface when the release of condensed dodecanol from the pores is accompanied by its substitution by air bubbles. The concurrent action of the two above-mentioned factors (i.e., the decrease in absolute value of wetting tension and the decrease in the roughness coefficient for the wetted area) causes a decrease in the value of the product $r_w (\sigma_{SV} - \sigma_{SL})$ for the second linear section in Fig. 3. This decreasing trend is continued at the third linear section due to dominating contribution of a decrease in the absolute value of wetting tension despite increase in the fraction of the wetted area. During this stage, corresponding to contact time between the droplet and the superhydrophobic substrate from 560 till 1460 min, the water/vapor interfacial tension increases and adsorption equilibrium is established between the bulk part of the droplet and the water/substrate interface, with an equilibrium value of the parameter $r_w (\sigma_{SV} - \sigma_{SL})$ equal to -47 mJ/m^2 and the fraction of wetted area about 9%. Note that even after 24 h of contact between the water droplet and the superhydrophobic substrate with the accumulated dodecanol, the aqueous droplet is still in the heterogeneous wetting mode, and the substrate retains the superhydrophobic state.

The data on f and $r_w (\sigma_{SV} - \sigma_{SL})$ obtained for the experiments of type 4 with the superhydrophobic substrate textured by anodic oxidation shows the similar evolution of the parameters of three-phase equilibrium. The different behavior of the parameters was observed in the experiments of type 1 and 3 (Table 2), where an essential temporal increase in the fraction of the wetted area is accompanied by an increase in $r_w (\sigma_{SV} - \sigma_{SL})$ values. Such difference may be related to the deficiency of dodecanol accumulated inside the pores upon exposure to dodecanol vapors at $T=25 \text{ }^\circ\text{C}$. The redistribution of dodecanol within the system during long-term contact with the droplet and its intense adsorption at

substrate/droplet interface at high values of droplet surface tension will cause partial pore filling with water. In turn, for parallel pore structure, the pore filling is accompanied by an increase in the roughness coefficient for the wetted part of the substrate and thus by an increase in the absolute value of $r_w(\sigma_{SV} - \sigma_{SL})$. Such phenomena favor the preservation of very high values of apparent contact angles despite essential increase in the fraction of the wetted area. Overall, the behavior of contact angles and the parameters of three phase contact for all types of the experiments with the superhydrophobic substrate obtained on the basis of anodic oxidation convincingly shows the high stability of the superhydrophobic state in contact with dodecanol vapors.

Table 2. Analysis of data on the wettability of superhydrophobic surfaces on the basis of Eq. (1)

Method of surface texturing	Type of experiment	Three-phase contact parameters	Linear section		
			I	II	III
Anodic oxidation	Type 1	Contact time interval, min	5-79	87-327	343-1015
		Fraction of wetted area, f	0.09	0.14	0.39
		$r_w(\sigma_{SV} - \sigma_{SL}), \text{ mJ/m}^2$	- 43	- 51	- 64
	Type 2	Contact time interval, min	2-12	13-143	560-1460
		Fraction of wetted area, f	0.06	0.02	0.09
		$r_w(\sigma_{SV} - \sigma_{SL}), \text{ mJ/m}^2$	- 54	- 50	- 47
	Type 3	Contact time interval, min	54-88	90-773	793-1233
		Fraction of wetted area, f	0.06	0.09	0.11
		$r_w(\sigma_{SV} - \sigma_{SL}), \text{ mJ/m}^2$	- 45	- 48	- 50
	Type 4	Contact time interval, min	40-118	128-1168	-
		Fraction of wetted area, f	0.05	0.02	
		$r_w(\sigma_{SV} - \sigma_{SL}), \text{ mJ/m}^2$	- 52	- 46	
Laser texturing	Type 1	Contact time interval, min	1-50	70-470	590-1390
		Fraction of wetted area, f	0.006	0.16	0.32
		$r_w(\sigma_{SV} - \sigma_{SL}), \text{ mJ/m}^2$	- 0.8	- 19	- 68
	Type 2	Contact time interval, min	0-4	27-136	144-1424
		Fraction of wetted area, f	0.06	0.07	0.3
		$r_w(\sigma_{SV} - \sigma_{SL}), \text{ mJ/m}^2$	- 55	- 53	- 68
	Type 3	Contact time interval, min	14-50	52-66	73-1480
		Fraction of wetted area, f	0.07	0.04	0.18
		$r_w(\sigma_{SV} - \sigma_{SL}), \text{ mJ/m}^2$	- 40	- 30	- 54
	Type 4	Contact time interval, min	34-99	107-1067	
		Fraction of wetted area, f	0.03	0.007	
		$r_w(\sigma_{SV} - \sigma_{SL}), \text{ mJ/m}^2$	- 57	- 30	

Now let us consider the behavior of superhydrophobic substrates designed by nanosecond laser texturing during four abovementioned types of experiment on contact with dodecanol vapors. Corresponding dependences of the contact angles and droplet surface tension versus time of contact between the superhydrophobic substrate and water droplet are shown in Fig. 4. The morphology of laser textured surface is significantly different from that for sample textured by anodic oxidation (Fig. 1). Laser textured surface possesses a broader distribution of pore sizes, with a large fraction of both significantly narrower and notably wider pores compared to anodic textured sample. Therefore, the laser textured samples may accumulate a larger amount of dodecanol in surface pores. Pore size distribution influences also the dodecanol vapor pressure in the experimental cell during long-term contact with aqueous droplets and the decrease in droplet surface tension. However, the general behavior of both the contact angle and the surface tension is similar to that discussed above for the substrate textured by anodic oxidation indicating high stability of the superhydrophobic state in

conditions of dodecanol vapor adsorption onto water/vapor and water/substrate interfaces. It is interesting to consider in more detail the behavior of the contact angle and surface tension of water droplet atop of laser textured substrate in continuous contact with dodecanol vapor (type 4 of the experiment, curves 4 in Fig. 4). For that, we again replot the data as $\cos\theta$ versus $1/\sigma_{LV}$ (Fig. 5).

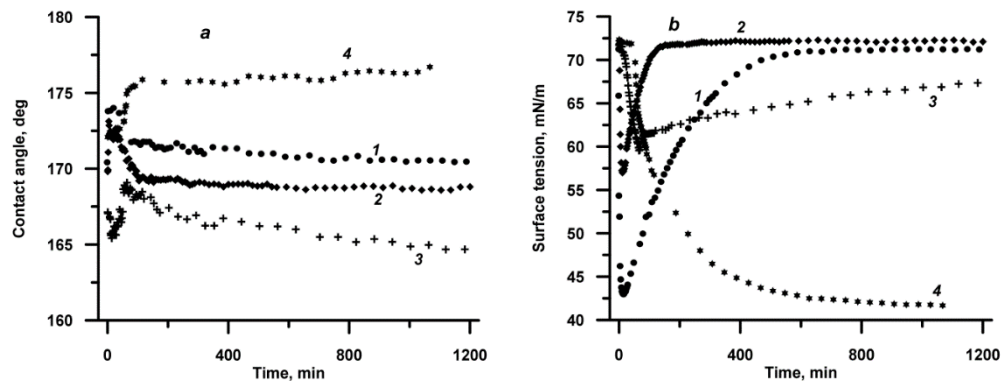


Fig. 4. Evolution in time of the contact angle (a) and the surface tension (b) of the aqueous droplet placed on the surface of the superhydrophobic AMG2 aluminum alloy substrate textured by nanosecond laser treatment, in four different modes of presence of dodecanol in the system: (1) the substrate was exposed to dodecanol vapors at 25 °C for 1 h; (2) the substrate was exposed to dodecanol vapors at 30 °C for 30 min; (3) the source of dodecanol vapors (the bowl with liquid dodecanol) was placed for 1 h inside the experimental cell with the substrate and sessile aqueous droplet and then taken off the cell; (4) the source of dodecanol vapors was present inside the experimental cell for the whole duration of the experiment

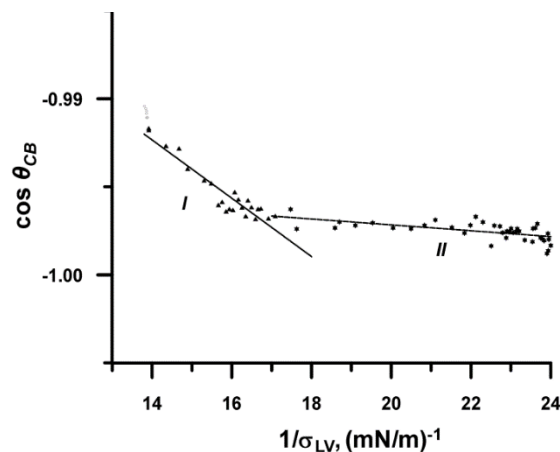


Fig. 5. Analysis of wettability evolution on the basis of Eq. (1) for an aqueous droplet on the superhydrophobic AMG2 aluminum alloy substrate textured by nanosecond laser treatment. The source of dodecanol vapors (the bowl with liquid dodecanol) was present inside the experimental cell for the whole duration of the experiment (experimental conditions of type 4). Symbols are experimental points, different symbols were used for points, assigned to different sections showing linear behavior; the lines show corresponding linear fits

Data presented in Fig. 5 allow selecting two sections well approximated by straight lines, indicating that two sets of stationary values of f and $r_w(\sigma_{SV} - \sigma_{SL})$ may be chosen for the corresponding time intervals (Table 2). The values of the fraction of the wetted area $f=0.007$ and of the product $r_w(\sigma_{SV} - \sigma_{SL})=30$ mJ/m², allow concluding that the adsorption of dodecanol molecules onto water/solid interface is significant. However, due to very low water droplet surface tension ($\sigma_{LV}=43$ mN/m), for the mentioned value of $r_w(\sigma_{SV} - \sigma_{SL})$ the fraction of wetted area retains exceptionally low value and the contact angle is higher than 175° even after 24 h of contact of the droplet with the superhydrophobic substrate. At the end of the experiment, the roll-off angle for testing droplet appeared to be 2.2°. Thus, the contact angle, the roll-off angle, and the fraction of the wetted area altogether unambiguously indicate heterogeneous wetting regime after long-term contact of a water droplet with the substrate in

the atmosphere saturated with dodecanol vapors. These data well correlate with the weak influence of n-hexanol and n-octanol on the wettability of the mixed inorganic-organic superhydrophobic coating by water (Krasowska et al., 2011).

4. Conclusions

In this study, we have analyzed the influence of dodecanol, as a representative of insoluble and low volatile surfactants, on the stability of the superhydrophobic state of coatings to long-term contact with water. The analysis was performed on the basis of monitoring the evolution of the sessile droplet parameters in a time of contact with a superhydrophobic substrate. To get a complete information, we have used two types of superhydrophobic coatings with very different morphology. Since our main purpose was to estimate the resistivity of superhydrophobic coatings to airborne organic contaminations at ambient exploitation conditions, we have modelled different regimes of interaction of tested superhydrophobic coatings with dodecanol vapors, including preliminary condensation of dodecanol inside the substrate pores/grooves at different temperatures, a short-term contact of dodecanol vapor with the superhydrophobic coating with deposited water droplets and, finally, a continuous 24 h contact between the substrate with deposited water droplets and the vapor phase saturated with dodecanol vapor. Although for both considered superhydrophobic coatings and at all regimes of contact with dodecanol, the continuous dodecanol adsorption onto substrate/water interface beneath the droplet was detected, the values of a fraction of wetted area unambiguously indicate the retention of the heterogeneous wetting regime. Overall, the variation of the contact angles upon contact of coating with a water droplet, and the roll-off angles measured after 24 h of continuous contact of the droplet with the substrate evidence good persistence of superhydrophobic state in conditions of contact with long-chain alcohol vapors.

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