Analysis of Long-Term Durability of Superhydrophobic Properties under Continuous Contact with Water

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ABSTRACT In view of more and more extending areas of application of hydrophobic and superhydrophobic materials and coatings, the problem of degradation of superhydrophobic state becomes extremely important. In this paper, the results of studies of time evolution of water contact angle on some siloxane-based hydrophobic and superhydrophobic surfaces in the conditions of long-term continuous contact with water are presented. Different mechanisms responsible for reversible and nonreversible deterioration of contact angle values were discussed and experimentally verified. We noted that evolution of water contact angle in time in the conditions of continuous contact with water needs to be considered when studying the durability of superhydrophobic coating because of its high sensitivity to the state of the coating and the details of its chemical structure.

KEYWORDS: superhydrophobic • durability • coating • siloxane based polymers • wetting • hydrophobicity degradation • contact angle

INTRODUCTION

Superhydrophobic surfaces have drawn a lot of interest in both academia and industry because of their applications as corrosion protective coatings, in preventing the adhesion of water and snow to windows or antennas, in enhancing buoyancy, and for many other purposes. However, there are only a few studies in the literature where the durability of superhydrophobic properties under continuous contact with water was investigated (1−6) and the mechanisms of degradation of superhydrophobicity were discussed. At the same time, the evolution of the contact angle of the material in continuous contact with aqueous media is of primary importance for revealing the possible areas of application of such superhydrophobic materials and coatings. This point becomes especially intriguing because in many cases the superhydrophobic (superlyophobic) state of the surface can appear as a relatively robust but metastable state (7, 8). The other important point is related to retention of the superhydrophobic state in the conditions of weak interaction between water and the constituents of hydrophobic surface. The necessity of the analysis of dynamics of wetting angles becomes evident if one takes into account that such interaction always exists, at least because of physical van der Waals interactions, but in many cases because of chemical types of interactions as well.

Here we present the analysis of the evolution of water contact angle on several siloxane-based hydrophobic and superhydrophobic surfaces over time under conditions of continuous contact with water. It will be shown that the dynamics of wetting is very sensitive to the state of the coating and the details of its chemical structure. We will discuss the reasons for the hydrophobicity depression and factors influencing the degradation of superhydrophobic properties.

MATERIALS AND COATING PROCEDURE

Glass coverslips used for the preparation of smooth hydrophobic coatings were purchased from “Klinsteklo” (Russia). rms roughness of surface for coverslips was 0.05 μm. Siloxane rubber P3303 (based on polydimethylsiloxane) from Penta was used as a substrate for superhydrophobic coatings. The same hydrophobic agent 1-(3-((2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)-oxy)propyl)-*N*,*N*,*N*-trimethylsilanetriamine, synthesized by Professor Muzafarov as described in ref 9, was used to prepare both the smooth hydrophobic coatings on glass and textured superhydrophobic coatings on rubber.

The motivation of such choice of materials for investigation is the following. Siloxane rubber is one of the most widely used in technology hydrophobic materials, for example, in the production of electric insulators. At the same time, its interaction with water is poorly studied despite the well-known fact of loss of insulating performance in damp air and at the atmospheric precipitations. The hydrophobic agent, used in our study, although newly synthesized, has a very high potential for technological applications because it is cheap, provides high values of contact angle being deposited on substrates, and reveals chemical affinity to many engineering materials, securing high adhesion of coating to the material surface. One more advantage of this chemical is related to the fact that it can be used simultaneously as a hydrophobic material and as a binder for filling agent in the process of formation of nanocomposite superhydrophobic coating.

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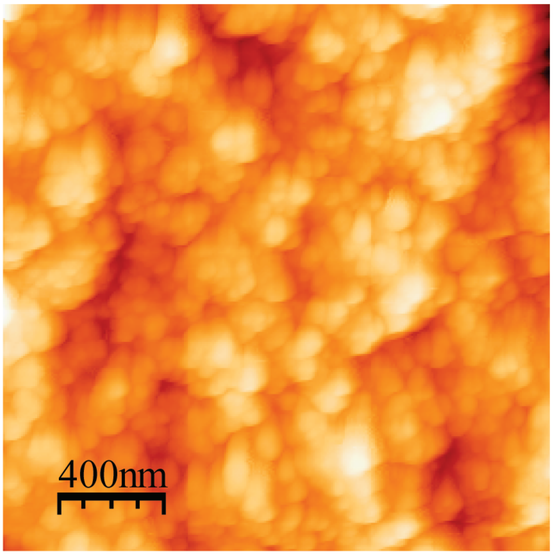

FIGURE 1. AFM image of superhydrophobic coating on surface of siloxane rubber P3303. The images were obtained using a MultiMode atomic-force microscope with a Nanoscope IV controller (Veeco, USA) in the tapping mode.

Before studying the dynamics of wetting and before deposition of coatings, glass coverslips and rubber samples were doubly kept for 30 min in distilled ethyl alcohol with changing of the solvent, and were then treated in an ultrasonic bath in 99.9% ethyl alcohol (from Merck) and three times in tridistilled water for 5 min, dried with an ash-free filter, and retained in a dry atmosphere for 16 h. To form the hydrophobic coating on glass slides, we deposited a wetting film of 2% solution of hydrophobic agent in 99% decane (Acros Organics) by the immersion method. After evaporation of solvent and cross-linking of hydrophobic agent, a smooth polymer film was formed on the surface of glass slide. The thickness of these films varied in the 20−30 nm range.

To produce the superhydrophobic coating, we dispersed Aerosil nanoparticles in volatile dispersion medium with hydrophobic agent dissolved. The wetting film of the dispersion was deposited onto the substrate, followed by evaporation of solvent at ambient conditions. It was shown (9, 10) that this method allows one to meet two conditions necessary to achieve the superhydrophobic state of the surface. Namely, low surface energy of the coating is provided by the hydrophobic agent and the heterogeneous regime of wetting is secured by the multimodality of roughness because of aggregation of Aerosil nanoparticles. The typical AFM image of the coating is shown in Figure 1. The multimodality of roughness is determined by characteristic length scales related to particle sizes on the order of 100 nm, aggregate sizes on the order of micrometers, and interaggregate distances on the order of portions of micrometers.

The application of the above hydrophobic agent allows one to not only decrease the surface energy of coating but at the same time use it as a binder of a coating to the substrate and as a binder between nanoparticles. The cross-linking of coating takes place through reaction of the hydrophobic agent with water molecules from the atmosphere, whereas binding to the substrate surface and to the surface of Aerosil nanoparticles occurs through the reaction of hydrophobic agent with surface hydroxyl groups. By adjusting the composition, viscosity, and volatility of dispersion medium, one can control the thickness of superhydrophobic coating, which is in the range of 1−3 μm.

Contact Angle Measurements. The study of the degree of hydrophobicity for the deposited coatings and its degradation was based on contact angle measurements. For this purpose, we have used the method of digital video image processing of a sessile drop of the test liquid on the investigated surface. The homemade experimental setup for obtaining the optical images of sessile drops and software for subsequent determination of drop parameters using Laplace curve fitting routine were described earlier (11, 12). A monochrome digital camera Pixelink PL-B686MU with space resolution 1280 × 1024, color resolution 256 gray levels, and time resolution 25 frames per second was used to capture the drop images. To analyze the deterioration of hydrophobic state, we used deionized water as a testing liquid. Such choice of the liquid allows studying the evolution of contact angle and the process of interaction of substrate with water in situ. The typical amount of time necessary for equilibrating the initial shape of deposited drop does not exceed milliseconds, and in the following, we will refer to the angle obtained in 2 s after the drop deposition as an initial wetting angle. The measured contact angles, as follows from the behavior of contact diameter, correspond to advancing contact angles. Subsequent evolution of drop shape is determined by many factors such as pinning of contact line in drop spreading over rough surfaces, growth of precursor adsorption or wetting film in the vicinity of drop, transition from metastable to stable regime of wetting, and interaction of liquid with substrate resulting in variation of wetting due to alteration of chemical composition of substrate.

To characterize the wetting of coatings, we measured initial contact angles in three to five various points on the surface of each sample, with an average angle for 10 consecutive images of the drop being defined for each place. The accuracy of contact angle determination was not worse than 0.1° for all angles measured on various substrates and was defined as the root-mean-square (rms) deviation of angles for 10 consecutive images of the drop.

Two independent methods have been used to study the long-term influence of substrate/water interactions on substrate wettability. In the first one (hereinafter method I) the evolution of water drop contact angle was studied as a function of time of drop contact with the substrate. In the second approach (method II), the sample was soaked in water for a long time. After a definite time of immersion, the sample was taken off the water, dried with an ash-free filter, and retained in a dry atmosphere for 16 h. The long-term wetting experiment was then performed in the same way as in method I.

To conduct measurements of the initial and contact-time-dependent contact angles and diameter of a drop, we placed a dry substrate inside the experimental cell on the top of fine positioner, allowing the adjustment of sample surface tilt with the accuracy 0.05°. The cell contained two water-vapor-saturated chambers inserted one into another in such a way that the pressure within each was equal to atmospheric, with 100% humidity inside the internal chamber and 98−99% humidity inside the external one. Although 100% humidity atmosphere has the vapor pressure undersaturated with respect to the convex drop surface, the water drop with a 2 mm contact diameter can be stored in such a system more than 1 month without noticeable evaporation-induced variation of diameter. The low evaporation rate and simultaneous measurement of contact angle and contact diameter made it possible to distinguish between the decrease in the contact angle caused by evaporation of the drop and that related to hydrophilization of the substrate as a result of its interaction with water.

To measure the rolling angle, we deposited the 10−15 μL drop onto the surface. After the initial drop shape equilibration, manipulating with the positioner allowed us to smoothly vary the inclination of the sample surface and detect the rolling angle.

RESULTS AND DISCUSSION

Smooth hydrophobic coatings, prepared as described above, were characterized by contact angles which vary from sample to sample in the range 105−110° with angle rms deviation ±2° along the sample. Superhydrophobic coatings demonstrated the variation of initial angle in the range 158−173° with angle rms deviation ±3.5° along each sample. However, the analysis indicated that the shape of drops was axisymmetric with circular wetting line. Thus it can be concluded that the surface of our coatings can be considered as quite uniform in the length scale of order of drop diameter.

Both types of coatings demonstrated very good stability of hydrophobic properties under storing in a laboratory. The drop of contact angle for one year of storage in laboratory did not exceed 2° for all samples. The application of sessile drop of water as testing liquid gives very good opportunity to study both the instantaneous wettability and the character of interaction of aqueous media with the surface layers of underlying substrate on the basis of contact time dependence of contact angle. The progression of initial contact angle and rolling angle obtained by method II as a function of immersion time in deionized water is shown in Figure 2, and the contact time-dependent angles reflecting the deterioration of wetting at long-term continuous contact of superhydrophobic surface with water drop as obtained by method I are presented in Figure 3.

The first signs of degradation of superhydrophobic properties as indicated by behavior of initial (Figure 2) and contact time-dependent (Figure 3) contact angles and by rolling angles (Figure 2) reveal after a few days of exposition in water. As it follows from the comparison of data on Figures 2 and 3, the contact time behavior of angles is much more sensitive to deterioration of wetting than the initial angles or rolling angles, and the initial angles for samples dried after being immersed in water for a long time do not completely reflect the details of superhydrophobicity degradation. The reason for above phenomena will be discussed below. From Figure 3, it may be concluded that increasing the time of preliminary immersion of a superhydrophobic surface in bulk water facilitates the deterioration of contact angle values in subsequent experiments on dynamics of wetting of water drop on the coating.

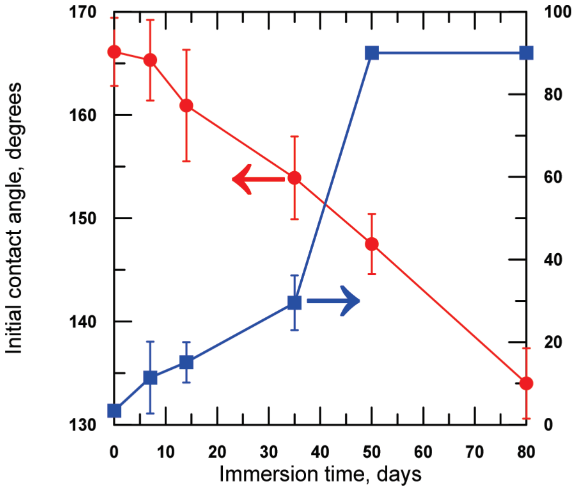

FIGURE 2. Contact and rolling angles of superhydrophobic samples as a function of immersion time in deionized water.

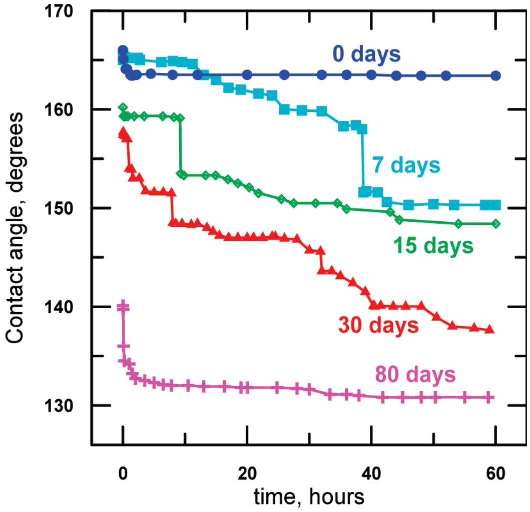

FIGURE 3. Time evolution of contact angle at continuous contact of water drop with superhydrophobic coating on siloxane rubber after different time (as indicated at the curves) of preliminary immersion in bulk water.

The following mechanisms may be considered as responsible for the above behavior. The first one is a growth of adsorption/wetting films on the substrate surface in the vicinity of drop, initiated on the one hand by increased vapor pressure near the convex drop, on the other hand by physical (van der Waals) and chemical (of various types) interactions. The second one is the surface hydrophilization due to chemical interaction such as the hydrolysis of free methylamine end groups and hydration of all active sites tending to create hydrogen bonds, like oxygen atom in the backbone of fluorooxysilane or polydimethylsiloxane in siloxane rubber, hydroxyl end group, and so on. Such

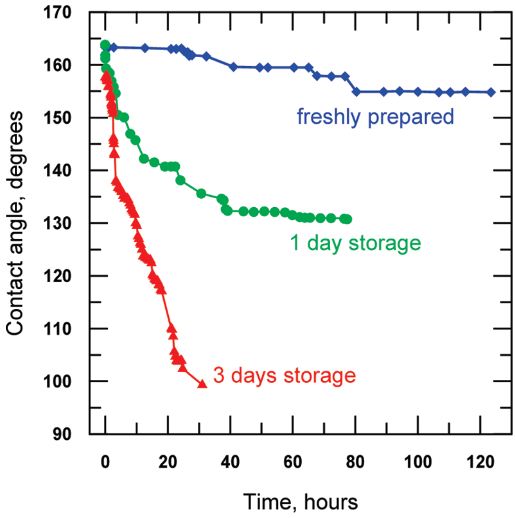

FIGURE 4. Time evolution of contact angle on superhydrophobic coatings, obtained after different time of dispersion storage at ambient conditions before deposition of coating.

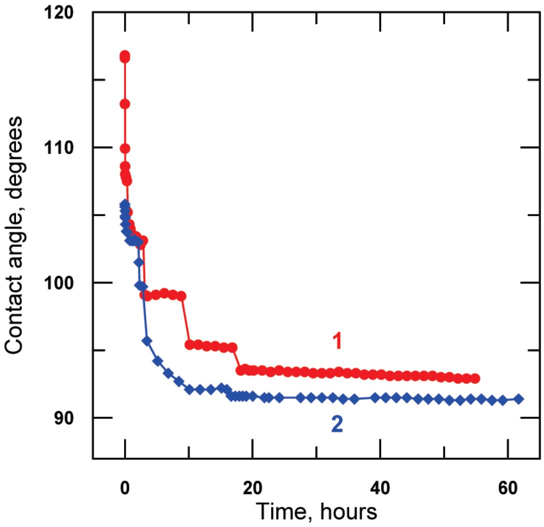

FIGURE 5. Evolution of dynamic contact angles for water drop on hydrophobic surfaces. 1, siloxane rubber; 2, smooth film of hydrophobic agent, deposited on glass slide.

interaction leads to increasing affinity of superhydrophobic coating to water and to contact angle decreasing.

The results of additional experiments on evolution of the contact angle on the series of superhydrophobic substrates produced as described above, but differing from each other by the portion of hydroxyl end groups appearing due to hydrolysis of free methylamine end groups, are shown in Figure 4. To achieve such modification of chemical composition of coating, we have varied the time of storage of dispersion with hydrophobic agent in contact with water vapors from atmosphere before the deposition of coating. As follows from the spectroscopic data on the behavior of bands of stretching vibrations of —OH and —NH— bonds, such storage is accompanied by the hydrolysis of part of the methylamine end groups.

Data in Figure 4 indicate that although the initial contact angle, provided by fluorocarbon tail of hydrophobic agent, is nearly the same for all coatings, the stronger the contact angle depression, the higher is the portion of hydroxyl groups, thus corroborating the significance of hydration processes of hydroxyl end groups in the degradation of hydrophobic properties. To study the role of hydration of some other active sites, tending to create hydrogen bonds (such as oxygen atoms), we performed additional experiments on hydrophobic surfaces.

The evolution of contact angles for water drop on smooth film of hydrophobic agent, deposited on glass slide from the freshly prepared solution, and on siloxane rubber surface is shown in Figure 5. The analysis of progression of contact angles indicates the significant deterioration of hydrophobicity which is interpreted in our study as a result of precursor wetting film formation and hydration induced hydrophilization of surface in contact with water drop. The growth of wetting/adsorption films from water vapor on hydrophobic and superhydrophobic surfaces was proved earlier by the measurement of surface resistance of hydrophobic and superhydrophobic materials in dry and water vapor saturated atmospheres (13). It was found (13) that the equilibrium film thickness is achieved, as a rule, during 2—5 h. The mechanism of hydrophobicity degradation associated to hydration of surface active sites tending to create hydrogen bonds in aqueous media correlates well with IR spectroscopy data. In spectroscopic experiment, it was found that OH stretching vibration band of water molecule at 3220 cm^{-1} (which can be assigned to hydrogen bonding to oxygen in polydimethylsiloxane backbone or/and to silanol groups) disappeared in the course of siloxane rubber film dehydration in the dried atmosphere of the spectrometer sample compartment. A much higher time of hydration, which amounts to days, in comparison to the time of dehydration on the order of 1 h indicates the significantly higher energetic barrier for the process of hydration than dehydration. We believe that namely this very quick process of dehydration of surface layer of superhydrophobic coating is responsible for the fact that the initial angles for samples being dried after soaking in water for a long time do not completely reflect the details of superhydrophobicity degradation.

It is interesting to note that the hydration of active sites tending to create hydrogen bonds results in swelling of surface layer of siloxane rubber (14). The analysis of evolution of contact angles for water drops on siloxane rubber and on film of hydrophobic agent deposited on glass substrate indicates that for both surfaces the total dynamic curves can be described by two stages. For the first stage, similar for both substances and completed within 2—3 h, the main mechanism of hydrophobicity depression is associated with wetting film formation. On the second stage, the main mechanism is related to hydration of surface hydrogen bonding active sites. The dissimilarity in details of dynamic curves on that stage results from the difference in surface topology. For rough siloxane rubber, the wetting line pinning is reflected in steplike character of the contact time dependence of the wetting angle.

SUMMARY AND CONCLUSIONS

We have presented the results of studies of time evolution of water contact angle on several siloxane-based hydrophobic and superhydrophobic surfaces in the conditions of continuous contact with water. Different mechanisms responsible for deterioration of contact angle values were discussed: (1) the growth of adsorption/wetting films, (2) the reversible hydration of active sites tending to create hydrogen bonds, (3) the hydrolysis of free methylamine end groups with their substitution by hydroxyl end groups, and finally, (4) the nonreversible hydration of hydrogen bonding active groups inside the hydrophobic and superhydrophobic material. The two former mechanisms cause the reversible deterioration of hydrophobicity, which can be restored by drying. The two latter mechanisms are responsible for irreversible degradation. We noted that the evolution of water contact angle in time (dynamics of wetting) in the conditions of continuous contact with water needs to be considered when studying the durability of superhydrophobic coating because of its high sensitivity to the state and details of the chemical structure of the coating.

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