MAKING OF SUPERHYDROPHOBIC SURFACES BY THE DEPOSITION OF NANOCOATIGS FROM SUPERCRITICAL CARBON DIOXIDE

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Abstract

The uniform coatings of fluorinated polymers were deposited from their solutions in supercritical carbon dioxide on a number of rough substrates. The superhydrophobic properties have been imparted to their surfaces, and, namely, to increase the value of the contact angle for water droplet to 130° and greater. The dynamics of changing of geometry of a drying droplet on a substrate is studied.

Introduction

Superhydrophobic surfaces are characterized by high values of water contact angles (up to 130° and greater) and a low hysteresis of contact angles. This allows for the easy removal of water droplets from these surfaces, together with particles of possible impurities. Such “self-cleaning” of superhydrophobic surfaces is termed “the lotus effect,” as it is analogous to the processes observed in lotus leaves[1]. It is known that the maximum contact angle for water on a smooth surface of hydrophobic materials does not exceed 120°. And also is known that the macroscopic hydrophobicity of the surface can be substantially enhanced through an increase in its roughness. The superhydrophobic properties of lotus leaves are explained precisely by the combination of nano- and microreliefs of the surface of crystallites of the hydrophobic paraffins that form the outer layer of the leaf.

Two main theoretical models were proposed to describe the interrelations between the hydrophobicity and roughness of the surfaces. The Wenzel model is true at low degrees of roughness[2], while the Cassie–Baxter model is valid at higher roughness[3]. The Wenzel formula makes is possible to describe an increase in the contact angle with increasing surface roughness by the following relation: $\cos \Xi = r \cos \Theta$, where Ξ is the contact angle on the rough surface, Θ is the contact angle on the smooth surface of the same material, and r is the roughness factor determined by the ratio of the areas of real surface and its geometric projection on the plane. The Cassie–Baxter formula gives an alternative variant for describing an increase in the contact angle on the rough surface compared to the smooth surface as follows: $\cos \Xi = -1+\varphi_s(1 + \cos \Theta)$, where φ_s determined as the fraction of surface coming into contact with the droplet of the wetting liquid, is introduced in place of the roughness factor. This definition implies that, as the surface roughness increases, the droplet of liquid no longer uniformly wets the surface at a certain moment (i.e., it wets both the local hills and valleys on the surface), but rests on the highest regions of the surface. The first (Wenzel) regime is characterized by the large value of hysteresis of the contact angle, that is, by the droplet sticking to the surface[4, 5]. The mechanism of the transition from Wenzel’s to Cassie’s regime has been described theoretically[6].

Thus, in order to produce an superhydrophobic surface, it is necessary to satisfy two conditions: (a) the surface should be rough (according to biomimetic approach, with the combination of nano- and microrelief) and (b) the surface material should by hydrophobic (the water contact angle on a smooth surface should exceed 90°). The condition (b) is necessary for the roughness to precisely increase the hydrophobic properties of a material (otherwise, according to Wenzel formula, we can obtain an "superhydrophobic" surface).

The method realized by us follows the scheme of the preparation of a superhydrophobic surface through the deposition of a uniform film of hydrophobizing agent from the solution in the supercritical carbon dioxide (sc-CO_2). We demonstrated earlier that one can form ultrathin (nanosized thickness) coatings with large degree of uniformity by depositing fluorinated polymer molecules from sc-CO_2 onto the atomically smooth surfaces of crystalline substrates of mica and highly oriented pyrolytic graphite[7–11].

Experimental

Materials

Ultradispersed polytetrafluoroethylene (UPTFE) FORUM (Fluoro-ORganic Ultradispersed Material, Institute of Chemistry, Far East Division, Russian Academy of Sciences, Russia) was chosen as the main hydrophobic polymer coating. This commercial material is the product of the thermal gas dynamic destruction of commercial polytetrafluoroethylene and consists of a mixture of low molecular weight and oligomeric perfluorinated linear chains, $(–CF_2–)_n$, with an average number of units, $n \approx 100$. We also used Teflon AF2400 copolymer (DuPont, US), poly(4,5-difluoro-2,2-bistrifluoromethyl-1,3-dioxole-*co*-tetrafluroethylene) with a content of dioxole groups of 87 mol%.

Various porous and rough materials, such as polymer track-etched membranes, microporous and composite polymer structures, porous woven and nonwoven materials, and nanostructured and crystalline surfaces were tested as substrates. In this work, we only report the results for substrates in which we succeeded in increasing the water contact angles to >130°, i.e., to a value exceeding the maximum attainable magnitude for smooth hydrophobic substrates.

Experimental Unit

High purity CO_2 (Linde Gas Rus, Russia, 99.995%) was transformed into the supercritical state (temperature above 31,1°C, pressure higher than 7,4 MPa) using a high-pressure unit schematically represented in Fig. 1. The unit consists of reaction cell *1* for the exposure of substrate *2*, liquid thermostat *3* for the stabilization of the temperature regime of exposure, valve system *4*, capillary lines *5* and manometers *6* for the supply of sc-CO_2 to the cell, manual pressure generator *7* for the transformation of CO_2 into the supercritical state, and cylinder *8* with CO_2.

Hydrophobization Procedure

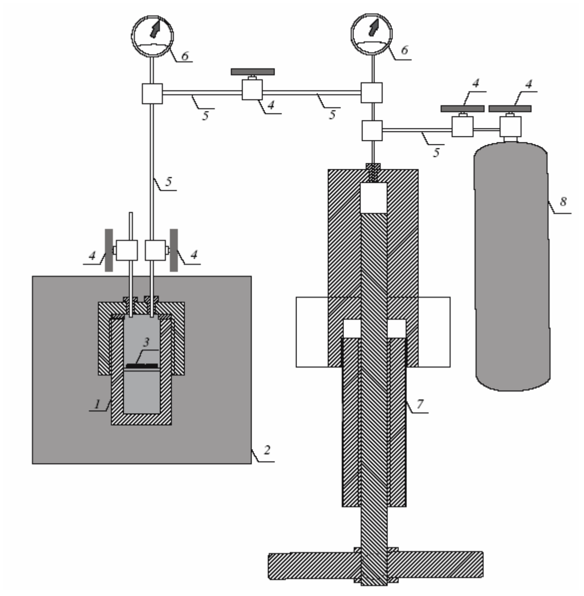
The modification of substrates was performed according to the following procedure using hydrophobizing agents. Prior to the experiment, a reaction cell with a volume of 10 ml was carefully and successively washed with various solvents, including sc-CO_2 at the final stage. Then, the substrate, subjected to exposure, with an area of about 1 cm^2 and a weighed polymer sample of the requisite mass, was placed into the cell. The polymer sample was preliminarily weighed with an Ohaus AP-250D (Ohaus, US) high precision analytical balance characterized by a standard measurement deviation of about 2×10^{-5} g. In the event of the complete dissolution or dispersion of polymeric material, the concentration of the solution or dispersion was determined by the ratio of the mass of weighed sample to the volume of the cell. The mass of the weighed sample was chosen so that the values of concentration fall on 0,01–0,1 g/l range. The cell was closed, sealed, and blown with CO_2 to remove traces of air and water. Afterwards, the requisite pressure at the given temperature was built up in the cell, which was placed into a liquid thermostat *3* using pressure generator *7* via capillary system *5* equipped with valves *4* and manometers *6* for pressure control. The temperature regime was established throughout the exposure process using an automatic system of temperature maintenance controlled by the thermostat. The sample exposure was performed over 2–4 h followed by cell decompression with CO_2 discharge. During the CO_2 discharge process, the cell temperature was maintained at a level exceeding the critical value of 31,1°C to prevent the formation of liquid CO_2 in the cell. The rate of CO_2 yield was 0,1-1 g/s. At high rates, the cell was cooled to a considerable extent owing to the effect of throttling (which could lead to the undesirable formation of liquid CO_2 phase in the cell, as well as to the condensation of moisture on the supercooled sample after the cell opening). Following decompression, the cell was dismantled and the modified substrate withdrawn; its hydrophobicity was investigated by measuring the contact angle with a Femtoscan Radian setup (Center of Advanced Technologies, Russia).

Within the framework of our study, we did not pose the problem of determining the boundaries of the solubility regions for hydrophobizing agents used in the sc-CO_2 (the boundary values of temperature and pressure). We only fixed the condition that the total or partial dissolution of a weighed sample of a given polymeric hydrophobizing agent can take place at the chosen experimental parameters (set by the temperature and pressure inside the cell). This was detected based on the absence of the hydrophobizing agent placed on the cell bottom at the onset of experiment after the completion of the sample's exposure, and its reprecipitation on the entire accessible surface area of the inner part of the cell.

The experiments performed demonstrated that superhydrophobicity may be induced in modified surfaces under the following conditions of exposure: at a temperature of 65°C, a pressure of 65 MPa, and an exposure time of 3 h. Decompression should be performed at 40°C at a rate of 0,5 g/s. In most cases, these parameters were used as the standards (designated below as the "standard conditions of exposure"). Slight variations in the temperature, pressure, and time of exposure, as well as in the temperature and rate of decompression around the aforementioned values within 10°C, 10 MPa, 1 h, and 0,1–1 g/s, respectively, did not noticeably affect the obtained numerical characteristics of the degree of superhydrophobicity (the measured values of the water contact angle). It was found, however, that at lower temperature and pressure values, the solubility of polymeric hydrophobizing agents in sc-CO_2 decreases. At lower decompression temperatures, CO_2 is transformed into a liquid state and its removal is accompanied by the negative effects of capillary forces on the deposited structures. At higher rates of decompression, the cell is overcooled due to the throttling effect, which can lead to the formation of liquid, or even solid, CO_2 in the cell, as well as potentially distorting the morphology of the deposited coatings.

Procedure for Measuring Contact Angles

A droplet of test liquid (water) with a volume of several microliters was placed on the substrate surface and the dynamics of its geometry measured over 1000 s (17 min) with a digital camera. In doing so, we measured the time dependences of the following geometric parameters of the droplet: the height h above the substrate, the diameter s of the contact zone with the substrate, and the contact angle θ using adapted software (see Fig. 2).



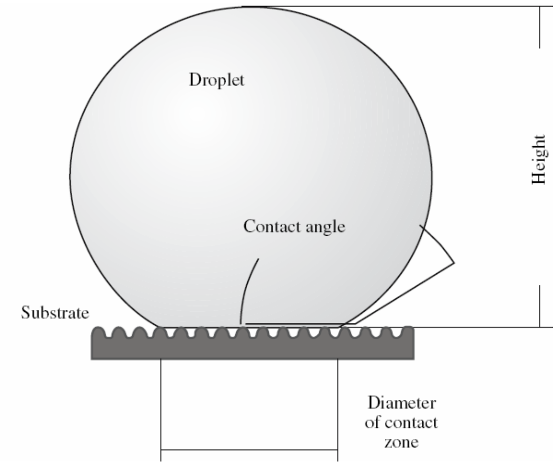


Fig. 1. Scheme of a high pressure unit for the deposition of coatings from solutions in sc-CO_2 on the substrate surface. *1*- reaction cell; *2*- liquid thermostat; *3*- exposed substrate; *4*- valves; *5*- capillaries; *6*- manometers; *7*- plunger hand-operated pressure generator; and *8*- cylinder with CO_2.

Fig. 2. Measured geometric parameters of the sessile droplet on the substrate, where θ is the contact angle, *h* is the height above the substrate; and s is the diameter of the contact zone.

Results of the observations of the changes in the geometry of sessile droplets of water on the surfaces of substrates studied in the course of evaporation are in the table.

Substrate	Contact angle, deg		Surface area of the contact zone, cm^2	
	immediately after droplet deposition	at a 50% decrease in droplet volume	immediately after droplet deposition	at 50%-decrease in droplet volume
Paper	84	50	0,075	0,075
Paper with UPTFE coating	150	141	0,0095	0,0098
Nanostructured graphite substrate	153	143	0,015	0,015
Nanostructured graphite substrate with a UPTFE coating	158	154	0,009	0,007
Carbon fabric	119	50	0,032	0,065
Carbon fabric with a Teflon AF2400 coating	133	116	0,022	0,024

Results and Discussion

The problem of a uniform, profound hydrophobization of a paper surface has an important applied significance due to the demand for similar technology in the polygraphic industry, the production of photographic materials, etc. Therefore, it was of interest to us to apply the procedure for preparing uniform coating made of UPTFE Forum grade deposited from the sc-CO_2 onto surface of paper having porous structure, as well as to study its wettability by water. The surface modification of paper (Canon, office grade) was performed by depositing UPTFE from the sc-CO_2 under standard conditions (see above). After the deposition of hydrophobic UPTFE coating from sc-CO_2, the paper surface demonstrates superhydrophobic properties (the initial contact angle is ~150°). The comparison of the dynamics of the variations in droplet volumes on the surfaces of an initial (unmodified) sample of paper and nonsorbing material (PTFE) made it possible to conclude that the decrease detected in droplet volume is explained by both the evaporation of water and its penetration into the porous substrate.

Porous and rough carbon materials, being the components of filters, sorbents, gas diffusion layers, and electrodes, are widely used in industry, including in high technology. The important problem to be solved in many specific applications is the deposition of thin, uniform, functional polymeric coating e.g., (hydrophobic) onto the accessible surface of porous carbon material. In this case, the coating should not change the morphology and properties of a material (the porosity and the pore size distribution).

In connection with this, it seems interesting to apply the procedure for depositing uniform fluorine-containing coating from sc-CO_2 onto the surface of porous carbon nanomaterial (nanographite) prepared by plasma chemical synthesis from the gaseous phase. This material is a carbon film deposited onto the surface of silicon wafer and consists of nanosized crystallites of graphite[12, 13].

The results of the study of the water wetting of initial graphite and graphite hydrophobized by depositing UPTFE from sc-CO_2 are shown in the table. It can be seen from these results that water droplets on surfaces of initial nanographite demonstrated behavior with the presence of a pronounced hysteresis of the contact angle, whereas after the deposition of the hydrophobic coating, the behavior was without of significant hysteresis. No moisture penetration into the porous structure was revealed for the substrate made of nanographite with a UPTFE coating deposited.

Uniform and extensive hydrophobization of fabrics is an important task, not only for the textile industry, but also for solving a wider scope of problems, including the production technology of various separating and filtering systems, as well as for biomedical applications involving functional elastic woven materials with controlled specific permeability. We performed the hydrophobization of a number of woven materials, including an S-CCG5 conducting carbon fabric produced by a SAATI group (Italy) under standard conditions using a Teflon AF 2400 copolymer. The production company positioned this fabric as a component of gas diffusion layers for he cases where the combination of low density, high electronic conductivity, elasticity, and compressibility is necessary in a material. The results of the study of this material are summarized in the table. It turned out that the developed approach enables one to increase the hydrophobicity of carbon fabric and prevent the sorption of liquid water (in the absence of a coating, the fiber imbibes the water).

Conclusions

A method for producing superhydrophobic surfaces is proposed. The method consists of depositing hydrophobizing coatings from solutions in supercritical carbon dioxide onto a rough or porous substrate. This method was used to hydrophobize a number of model surfaces whose wetting (before and after the deposition of coatings) was studied by analyzing variations in the geometry of sessile droplet of water on the testing substrate. This made it possible to monitor the decrease in the effect of hydrophobicity in the extended contact between the substrate and sessile droplet, to estimate the wetting hysteresis, and to detect the sorption of a liquid by the porous substrate.

It was established that the developed method of hydrophobization allows for ultrahydrophobic and water-ultrarepellent properties to be imparted to paper and nanostructured carbon materials. In addition, we succeeded in developing superhydrophobic coatings on atomically smooth substrates.

Acknowledgments

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