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Wetting hysteresis induced by temperature changes: Supercooled water on hydrophobic surfaces

Golrokh Heydari [a,*], Maziar Sedighi Moghaddam [b,c], Mikko Tuominen [b], Matthew Fielden [d], Janne Haapanen [e], Jyrki M. Mäkelä [e], Per M. Claesson [a,b]

[a] KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemistry, Surface and Corrosion Science, Drottning Kristinas väg 51, SE-100 44 Stockholm, Sweden

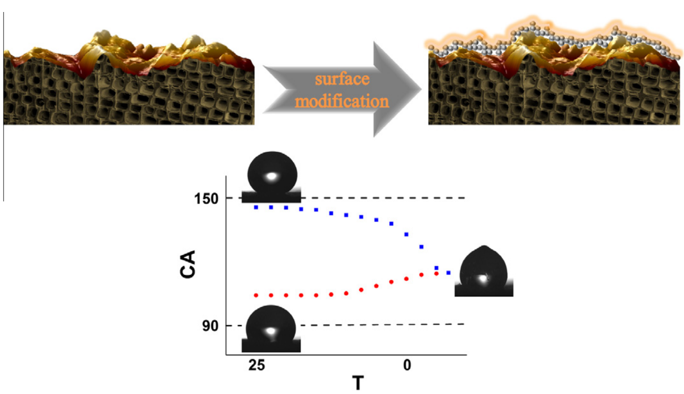
[b] SP Technical Research Institute of Sweden, Chemistry, Materials and Surfaces, Box 5607, SE-114 86 Stockholm, Sweden

[c] KTH Royal Institute of Technology, School of Architecture and the Built Environment, Department of Civil and Architectural Engineering, Building Materials, SE-100 44 Stockholm, Sweden

[d] KTH Royal Institute of Technology, School of Engineering Sciences, Department of Applied Physics, Nanostructure Physics, SE-106 91 Stockholm, Sweden

[e] TUT Tampere University of Technology, Aerosol Physics Laboratory, Department of Physics, P.O. Box 692, 33101 Tampere, Finland

GRAPHICAL ABSTRACT



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ABSTRACT

The state and stability of supercooled water on (super)hydrophobic surfaces is crucial for low temperature applications and it will affect anti-icing and de-icing properties. Surface characteristics such as topography and chemistry are expected to affect wetting hysteresis during temperature cycling experiments, and also the freezing delay of supercooled water. We utilized stochastically rough wood surfaces that were further modified to render them hydrophobic or superhydrophobic. Liquid flame spraying (LFS) was utilized to create a multi-scale roughness by depositing titanium dioxide nanoparticles. The coating was subsequently made non-polar by applying a thin plasma polymer layer. As flat reference samples modified silica surfaces with similar chemistries were utilized. With these substrates we test the hypothesis that superhydrophobic surfaces also should retard ice formation. Wetting hysteresis was evaluated using contact angle measurements during a freeze–thaw cycle from room temperature to freezing occurrence at −7 °C, and then back to room temperature. Further, the delay in freezing of supercooled water droplets was studied at temperatures of −4 °C and −7 °C. The hysteresis in contact angle observed during a cooling–heating cycle is found to be small on flat hydrophobic surfaces. However, significant changes in contact angles during a cooling–heating cycle are observed on the rough surfaces, with a higher contact angle observed on cooling compared to during the subsequent heating. Condensation and subsequent

* Corresponding author.
E-mail address: ghh@kth.se (G. Heydari).

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frost formation at sub-zero temperatures induce the hysteresis. The freezing delay data show that the flat surface is more efficient in enhancing the freezing delay than the rougher surfaces, which can be rationalized considering heterogeneous nucleation theory. Thus, our data suggests that molecular flat surfaces, rather than rough superhydrophobic surfaces, are beneficial for retarding ice formation under conditions that allow condensation and frost formation to occur.

1. Introduction

Wetting of hydrophobic surfaces by water has received significant attention in the last decades due to the use of (super)hydrophobic surfaces in different application, for example for controlling corrosion [1,2], adhesion [3], condensation [4], fouling [5], drag in microfluidic devices [6], and for achieving self-cleaning [7] properties. In addition, (super)hydrophobic surfaces have been suggested for anti-icing and de-icing purposes [8], requiring mechanical and wetting durability [9]. This could possibly offer a route to combat icing issues that are affecting everyday life as well as industrial applications [10]. We note that environmental conditions promoting condensation and frost formation on surfaces is common in most practical applications where icing is a problem, such as on roads and airplanes, heat exchangers, outdoor structures and buildings. Though a transition in wetting state of (super)hydrophobic surfaces could be desired and achieved by external stimuli [11–15] in some applications, it could be problematic for their function as anti-icing and de-icing coatings. Evaporation [16], pressure [17] and the kinetic energy of impinging droplets [18–21] can all induce the Cassie–Baxter [22] to Wenzel [23] state transition on structured superhydrophobic surfaces.

Due to the implication of superhydrophobic surfaces as being useful for combating ice formation [24–34] there is a need to study the effect of temperature on the wetting state of water droplets on such surfaces and possible transitions in wetting behavior induced by temperature cycling. Though a number of works have explored the influence of low temperatures and surface characteristics on interactions of sessile [26,35–39] or impinging [31,34,40] water droplets on (super)hydrophobic surfaces, only a limited number of reports address the robustness of the wetting state on superhydrophobic surfaces during cooling–heating cycles [41,42]. There is lack of understanding of how the surface roughness affects the wetting reversibility during temperature cycles relevant for anti-icing applications, especially during a freeze–thaw cycle where condensation and subsequently frost formation may affect wetting properties. We provide insight into this area by utilizing flat hydrophobized silica surfaces as well as stochastically rough hydrophobic and superhydrophobic wood surfaces having similar chemistry to elucidate topography effects. We note that stochastically rough surface, such as our wood samples, are relevant for practical applications, and there is an increased interest in utilization of wood in various constructions as sustainability issues are becoming more important. Though, surface modification of wood to restrict water penetration improve dimensional stability and biological degradation [43,44], its affect on the wetting properties during freeze–thaw cycles is not clarified despite being of importance for outdoor applications in cold climate regions. To our knowledge there is no previous report on interactions between modified wood surfaces and water at subzero temperatures.

Despite an increased number of scientific works devoted to heterogeneous nucleation of ice from supercooled water, there is still a discussion on whether there is a correlation between surface (super)hydrophobicity and anti-icing properties [7,27,28,30,31,33,45,46]. This is related to differences in experimental conditions such as temperature and relative humidity, heat transfer mechanisms, size of surface features and robustness of coatings in contact with water [26,47]. Many researchers report anti-icing properties, such as delayed freezing of supercooled water or higher degree of water supercooling, of hydrophobic and in particular superhydrophobic surfaces [24–33,45,48]. However, others report no or limited benefits of such surfaces [38,47,49]. In addition, in a few cases hydrophilic surfaces have been demonstrated to induce longer freezing delay times than hydrophobic ones [46,49,50].

It is not obvious how surface morphology will affect kinetics of ice formation even though ice nucleation should occur more readily on concave than convex sites [47]. How surface roughness affects freezing of supercooled water on surfaces with similar chemistry has been discussed in just a few recent works [24,28,31,47,51]. In the current manuscript we elucidate this topic in relation to temperature-wetting stability data. Our data show that the wetting hysteresis during a cooling–heating cycle (23–25 °C down to −7 °C and back to 23–25 °C) is smaller on flat hydrophobic surfaces than on rough ones with similar chemistry, even though introduction of small roughness features reduces the wetting hysteresis on rough surfaces. We demonstrate that (i) the observed wetting hysteresis is induced by condensation and frost formation at low temperatures, (ii) the coated surfaces are robust over several freeze–thaw cycles, and (iii) under conditions when condensation and frost formation occurs the freezing delay of supercooled water on a flat surface is longer than on a rough surface with similar chemistry. This can be rationalized by considering classical heterogeneous nucleation theory. Thus, stochastically rough (super)hydrophobic surfaces do not appear to offer any anti-icing benefits compared to flat surfaces with similar chemistry during conditions of freezing and thawing in humid air.

2. Experimental section

2.1. Materials

The surface topography of stochastically rough wood surfaces was modified utilizing a thermal aerosol based technique, Liquid Flame Spray (LFS) [52,53], for depositing titania (TiO_2) nanoparticles. This adds sub-micro- and nano-roughness features to the wood surface that has roughness features predominantly on the micro scale. Subsequently, the surface chemistry of uncoated and TiO_2-LFS-coated wood was altered using cold plasma polymerization, which is a dry technique that previously has been utilized for surface modification of wood [43,54]. Silicone and fluorine containing monomers are appropriate for depositing hydrophobic coatings [43,55,56], and in this study we utilized hexamethyldisiloxane (HMDSO) and perfluorohexane (PFH) monomers to make a plasma polymerized hydrophobic layer. Flat silica surfaces were modified with the same plasma treatment. Water for sample preparation and experiments was purified utilizing a Milli-ROP1s unit connected to a Milli-Q plus 185 system, and filtered through a 0.2 μm Millipak filter. The purified water had resistivity of 18.2 MΩ cm and organic content of less than 3 ppb.

2.1.1. Wood surfaces

Kiln dried blocks of Scots pine (*Pinus sylvestris* L.) sapwood with dimensions of about 30 mm in the longitudinal (L) direction, 7 mm