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Icephobicity studies of superhydrophobic coatings on concrete via spray method

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ABSTRACT

Road icing has brought huge potential safety hazards and hundreds of millions of losses every year. However studies for anti-icing or de-icing coatings on concrete are still rare due to the special features of concrete surfaces. Here superhydrophobic coating was performed on concrete via spray method and the icephobicity was studied experimentally and theoretically. The low ice adhesive strength and good durability of sprayed coatings represent the potential for icephobic concrete and our theoretical model provides effective route for the design of icephobic concrete.

1. Introduction

In cold winter icing on roads, electrical wires, signboards and airplane wings is unavoidable and common almost in the whole world. The ice formation, accretion and adhesion caused transportation hazards including slippery roads, cracked concrete structures, flight cancellations/delays, resulting in significant casualties and economic losses [1]. Various approaches have been used for ice removal including mechanical equipment, electro-thermal system and antifreeze depressants. However, these ways would cause pavement damage, large energy consumption, or environmental pollution generally. Recently, superhydrophobic coatings have attracted much research interest for anti-icing owing to its low-cost, environmentally friendly and high efficiency [2]. Most studies exhibited that superhydrophobic surfaces could distinctly increase the freezing time (i.e. anti-icing) [3] and reduce the ice adhesion strength (i.e. icephobicity) [4]. However, most previous reported superhydrophobic coatings were built on glass, metallic substrates including steel [5], copper [6], titanium alloy [7], etc. There is rare study about superhydrophobic coatings on concrete substrates.

As an important basic material in civil engineering and construction fields, cement-based concrete is one kind of composites using cement as a binding agent and graded coarse and/or fine aggregate (stone, sand, etc.) as reinforcement. Compared with glass or metallic substrates, concrete surfaces not only have hierarchical rough structures, but also possess nano-, micro- and macro-pores which connect with interior. Thus the icing formation, adhesion or de-icing on concrete is much different from those on metallic substrates. So far as we know, only Arabzadeh [8] or Vivian [9] tested the water contact angle (CA) or coefficient of friction of superhydrophobic coating on concrete and Rahul Ramachandran [10] observed the linear correlation between water CA and ice adhesion strength (IAS) on concrete. The icephobic durability of superhydrophobic coatings on concrete has never studied even if it is very important. Therefore there is still a big challenge to design robust superhydrophobic coatings for icephobic concrete.

In this research, we used a two-step spray method for durable superhydrophobic coatings on concrete and the results show that the IAS of coated concrete is much lower than that of uncoated concrete. Theoretical model of IAS was proposed based on the hierarchical porous and rough surface character of concrete. Good durability was exhibited due to the bonding between concrete and superhydrophobic particles as well as the protection provided by the hierarchical porous surface of concrete.

2. Materials and methods

Standard concrete tiles of 40 mm × 40 mm × 20 mm were prepared for the hydrophobicity and icephobicity tests. The mixture

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design and details were shown in supplementary information. One kind of fluorine resin (FCB-024, Guangzhou Zhuangjie Chemical Co., Ltd) was diluted in acetone, which was firstly sprayed on the concrete tiles as the adhesive layer. After accelerated curing on a hot stage (60 °C) for 10 min, the superhydrophobic solution was then sprayed on the above sample as the superhydrophobic layer. The preparation of superhydrophobic solution using silica nanoparticles (particle size of ~300 nm) could be found in our previous work [11].

The static contact angles were measured using the Ramé-Hart standard automated goniometer (Model 290), and the roll-off angles (RA) were measured using a home-made tilting stage. The tests methods for water absorption, IAS and durability were shown in the supplementary information.

3. Results and discussion

The fabrication of robust superhydrophobic concrete is illustrated in Fig. 1 via facile two-step spray method. Here the diluted fluorine resin was sprayed on the concrete to act as the adhesive layer, improving the durability of superhydrophobic coating. In our previous work, fluorosilane functionalized silica (F-SiO_2) nanoparticles were fabricated and suspended in isopropanol (IPA) [11]. F-SiO_2 solution was sprayed on the fluorine resin-coated concrete to be the superhydrophobic layer. Fig. 1d shows the SEM image of pristine concrete surface, indicating the multi-scale porous (from tens of micrometers to tens of nanometers) and rough structure. In comparison, the SEM image of the superhydrophobic coating (Fig. 1e) exhibited loose nanoporous structure with ~50 nm particles. The thickness of superhydrophobic coating is about several hundreds of nanometers, thus the multi-scale roughness of concrete surface remains after the coating process.

Fig. 2a shows the huge water contact angle change on pristine concrete, i.e., from 57.5° at the beginning to 18° at 840 s and completely spreading at last. It suggests that water interpenetrates into interior of concrete due to open pores on the surface. This is different with surfaces of glass, metals or ceramics. Here, the apparent contact angle of concrete is defined as the tested contact angle at 10 s for further studies. Fig. 2b illustrates the water CA and RA on concrete after spraying different times. It indicates that a continuous coating could be formed after two-time spray. Here we sprayed three times of superhydrophobic layer on each concrete without any special instruction. The CA of 165.5° and RA of 1.5° suggest an excellent superhydrophobicity.

The ice formation process was simply observed via dropping cooling water on the cold concrete. As illustrated in Fig. 3a, once water droplets contact with uncoated concrete, spread on the surface and then form the ice pieces in 5 s. In contrast, water droplets turn into spherical on coated concrete even at low temperature. With the heat transfer from water to the concrete, the spherical droplets turn into ice balls (Fig. 3b inset). With the propagation of ice balls, the ice layer forms on the surface of coated concrete (Fig. 3b). The ice layer could be easily removed, and the ice interface is very smooth seen from Fig. 3b inset.

As shown in Fig. 3d, the IAS of coated concrete (E_s) is about one tenth of that of pristine concrete (E_c). However, according to the previous theoretical formula, the IAS ratio is about 1/30, and the details were shown in support information [4]. Here we define the whole IAS $E = E_1 + E_2$, where E_1 and E_2 represent the contribution due to surface roughness and open pores, respectively. Through the calculation in the support information, we could get: $E_{s2} = 2.3 \cdot E_{s1}$ and $E_{c2} = 0.1 \cdot E_{c1}$. Thus the ice adhesion of coated concrete is mainly from the contribution of open pores. Therefore, the icephobicity of coated concrete could be greatly improved if the open pores are clogged by superhydrophobic particles.

Fig. 3e demonstrates that there is no remarkable increase of ice adhesion strength of coated concrete when the icing-deicing is less than thirty times. Moreover, the coated concrete surface remains superhydrophobic. The good durability of icephobic coating proves that the excellent interfacial bonding between the concrete and superhydrophobic coatings due to the resin layer. In addition, we think the hierarchical rough concrete offers a cushion effect to enhance the mechanical durability of superhydrophobic coatings. More, the low ice adhesion strength results in the ease of deicing process during shear tests without compromising the adhesive and superhydrophobic coatings. While with the increase of icing-deicing process, the coatings start to be destroyed especially during the deicing process.

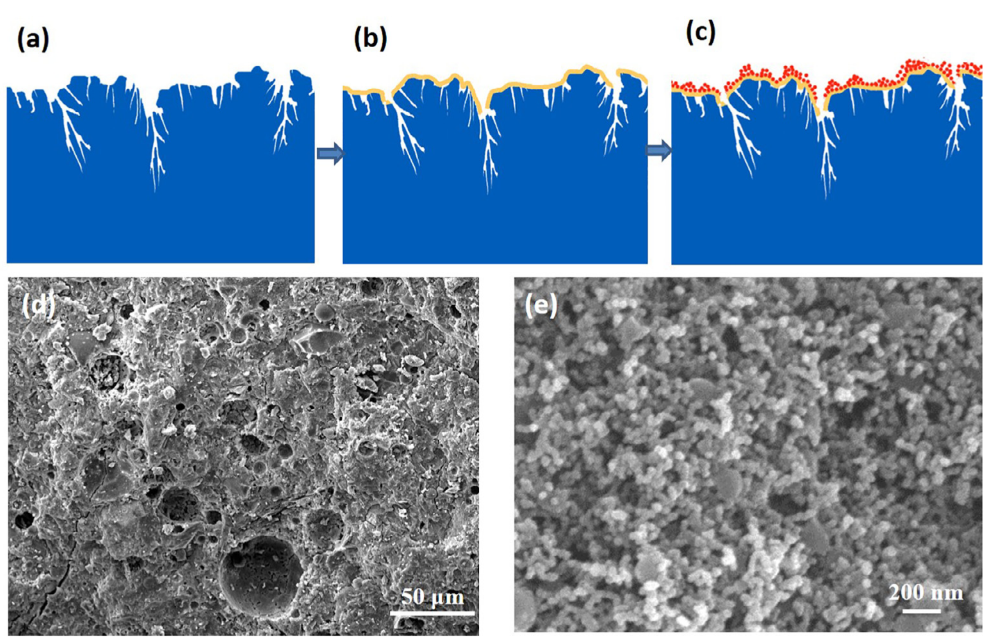

Fig. 1. (a–c) Schematic illustration of the formation of robust superhydrophobic coating on concrete via spray method. (d) SEM images of pristine concrete surface and (e) superhydrophobic coatings on concrete.

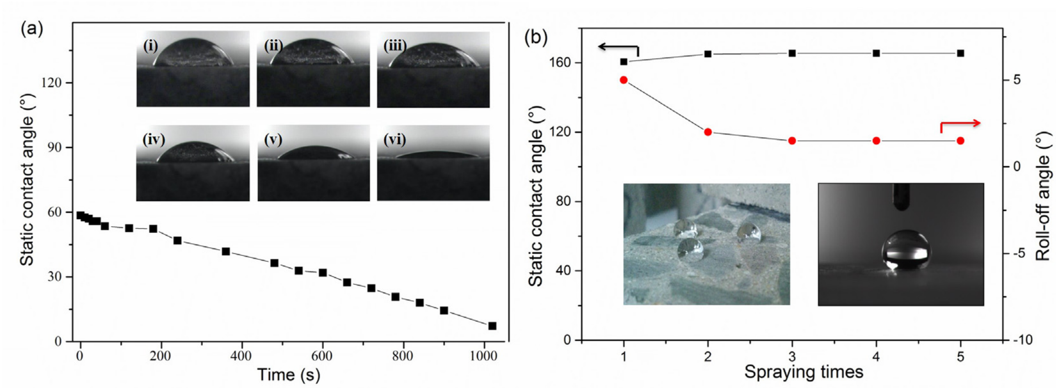

Fig. 2. (a) Water contact angles change on pristine concrete with different time. Inset: Typical images of water droplets on pristine concrete at (i) 10 s, (ii) 60 s, (iii) 120 s, (iv) 240 s, (v) 540 s and (vi) 840 s. (b) Water static contact angles and roll-off angles of coated concrete with different spray time of superhydrophobic layer. Inset: Typical optical images of water droplet on coated concrete.

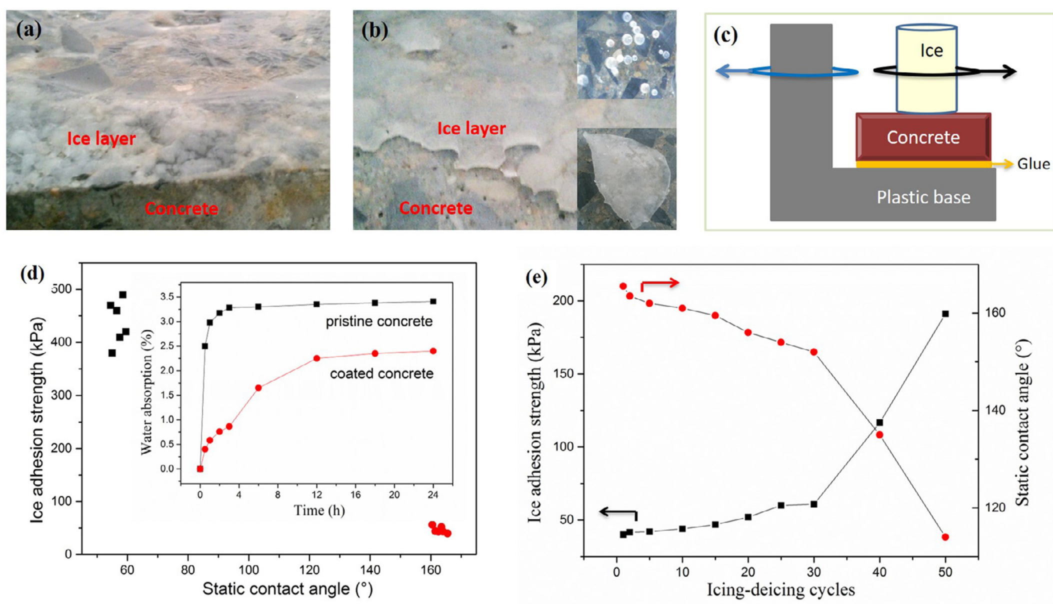

Fig. 3. The ice formation on (a) uncoated and (b) coated concrete at −20 °C. Inset: formation of ice balls at the beginning of icing (top) and the ice piece after removing (bottom). (c) The schematic illustration of set up for the shear tests. (d) The water contact angles and IAS of uncoated and coated concrete. Inset: the water absorption of coated and uncoated concrete. (e) The durability of coated concrete with different icing-deicing time.

4. Conclusions

Great importance of icephobic concrete has been shown due to the transportation safety and financial reasons. Here we reported a two-step spray approach for durable, superhydrophobic coatings on concrete. The ice adhesive strength of coated concrete was much lower after coating. Moreover, a theoretical model for coated and uncoated concrete was set up for the first time based on the hierarchical rough and porous surface of concrete. Good icephobicity of coated concrete within 30 icing-deicing cycles suggests high durability of two-step sprayed coatings.

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