Fabrication and anti-frosting performance of super hydrophobic coating based on modified nano-sized calcium carbonate and ordinary polyacrylate

Hao Wang a, Liming Tang a,*, Xiaomin Wu b, Wantian Dai b, Yipeng Qiu a

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
Department of Thermal Engineering, Tsinghua University, Beijing 100084, China

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Abstract

Nano-sized calcium carbonate (CaCO₃) particles were modified by heptadecafluorodecyl trimethoxysilane under acidic water condition. An ordinary polyacrylate prepared via radical copolymerization of methyl methacrylate, butyl acrylate, acrylic acid and β-hydroxyethyl methacrylate was used as the binder to form hydrophobic coatings with the modified CaCO₃. Super hydrophobic coating with water contact angle of 155° was obtained from modified CaCO₃ and the polyacrylate at their weight ratio of 8/2 by a simple procedure. Based on surface analysis by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS), the super hydrophobicity can be attributed to both the surface microstructure and surface enrichment of fluoroalkyl chains. Due to a low water sliding angle, carbon black powder on super hydrophobic surface was easily removed by rolling water droplet. Furthermore, the anti-frosting performance of different surfaces was investigated, which indicated that the frost formed on superhydrophobic surface was greatly retarded compared with that on bare copper surface. The surface kept superhydrophobicity even after freezing–thawing treatment for 10 times.

Keywords: Super hydrophobic coating; Nano-calcium carbonate; Polyacrylate; Anti-frosting performance

1. Introduction

Superhydrophobic surfaces with water contact angle higher than 150° have gained special attention these years due to their unique properties and many potential applications [1]. Because of their rather high hydrophobicity, such surfaces possess some interesting characters, such as low water and snow adhesion, low friction in surface dragging and easy removal of dirt [2–4]. In general, increasing surface roughness and decreasing surface energy of the surface material are two ways to achieve super hydrophobicity [5]. In nature, “self-cleaning effect” is an important character for lotus leaf with super hydrophobicity, which can be attributed to the surface roughness and the wax-like crystals on the top [6]. Up to now, many different techniques have been developed to prepare such surfaces [7–11]. Among them the use of nano-sized particles to increase surface roughness of a hydrophobic surface should be a practicable approach. For example, Chung et al. fabricated hydrophobic surfaces with the highest water contact angle of 135° using commercial silica particle and octyltriethoxy-silane in an aerosol spray reactor [12]. Daoud et al. prepared a series of hydrophobically modified silica nanocomposite coatings with the highest water contact angle of 141° by using a low temperature sol–gel process. Gu et al. synthesized organic–inorganic polymethacrylate (PMMA)/SiO₂/TiO₂ composite films with water contact angle over 100° by sol–gel processes [13]. Yan et al. reported a super hydrophobic coating based on nanometer CaCO₃ and PVDF in presence of tridecafluorooctyltriethoxysilane. The combination of microspheres of difference sizes makes the coating surface highly rough and porous in microscopic scales, leading to a high contact angle of 153° [2]. Hsieh et al. prepared various rough surfaces by using titanium oxide nanoparticiles and perfluoroalkyl methacrylic copolymer. The excellent water- and oil-repellence of the superhydrophobic nanostructured surfaces was ascribed to the increase of surface roughness and fluorinated-contained surface [14]. Kajiyama et al. prepared super-liquid-repellent surfaces by using sol–gel coating technology, in which the
colloidal silica nanoparticles and fluoroalkylsilane coupling agent were responsible for controlling roughness and surface energy [15]. From these results, it is noticed that superhydrophobic surfaces are generally obtained by using both nanoparticles and fluorinated reagents or polymers as the binder. Meanwhile, some of the techniques required complicated sol–gel processes, which are difficult to control from practical view point. Therefore it is desired that superhydrophobic surface can be prepared by a simple process, or even by using an ordinary polymer as the binder.

On the other hand, the formation of frosts on evaporator surface would plug up the air channel and decrease the working efficiency of many industrial devices, such as heating pumps, coolers, refrigerators and air conditioners. The utility of anti-frosting coatings in these devices should be an effective way to solve this problem. In our previous study, a hydrophobic fluoropolyacrylate coating with water contact angle of 100° was found to retard the formation of frosts on cold surface [16]. However, it is still not very clear how the anti-frosting performance changes in case of a more hydrophobic surface. Recently, we described the preliminary results of anti-frosting performance of superhydrophobic surface [17].

The purpose of this study is twofold: (1) the preparation of a superhydrophobic surface from modified nanoparticles and an ordinary polyacrylate, and (2) investigation the anti-frosting performance of surfaces with different hydrophobicity. Because the nanoparticles provide the surface with both high roughness and low surface free energy due to their exterior fluorochains, an ordinary polyacrylate can be used as the binder to achieve superhydrophobicity, therefore simplifying the preparing process.

In this paper, we designed a simple process to prepare superhydrophobic coating based on modified nano-sized CaCO₃ particles and an ordinary polyacrylate as the binder. The surface microstructures and the surface composition were investigated by SEM and XPS, respectively. The anti-frosting performance of superhydrophobic surface was compared with that of bare copper surface.

2. Materials and methods

2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA) and β-hydroxyethyl methacrylate (HEMA) (all in analytical grade) were purchased from Institute of Tianjin chemical reagent (China) and were used without further purification. Heptadecafluorodecyl trimethoxysilane (FAS-17, analytical grade) was purchased from Toshiba Silicone Co. (Japan). Nano-sized CaCO₃ with an average size of 40 nm was supplied by Shanghai chemical reagent factory (China). All the other reagents were all analytical grade.

2.2. Synthesis and characterization of polyacrylate

Polyacrylate was prepared through free radical polymerization of MMA, BA, AA and HEMA in butyl acetate with azodiisobutyronitrile (AIBN) as the initiator. 21.5 g MMA, 20.5 g BA, 1.5 g AA and 1.5 g HEMA were dissolved in 35 g butyl acetate. The solution was transferred into a 250 mL three-necked flask equipped with a mechanical stirrer, a dropping funnel and a condenser. A solution of 0.1 g AIBN in 5 g butyl acetate was added to the flask. Then the reaction temperature was elevated to 85 °C and the mixture was stirred at this temperature for 3 h. When a solution of 0.3 g AIBN in 5 g butyl acetate was added into the flask, the mixture was stirred for another 5 h to complete the reaction. The final concentration of the polymer solution was 50%. With tetrahydrofuran as eluant and at flow rate 1 mL/min, gel permeation chromatography (GPC, using a Waters 515 pump and a Waters 2410 DRI detector) analysis of the polymer gave the number average molecular weight of 79,860 and the polydispersity of 1.69. Differential scanning calorimetry (DSC) measurement carried out with a DuPont 2400 DSC Plus module at a heating rate of 10 °C/min gave only one T_g at 26.4 °C for the polymer. 1H NMR (Unity-200, 200 MHz, CDCl₃, δ): 0.95 (–CH₃CH₂CH₂CH₂CH₃), 1.38 (–CH₂CH₂CH₂CH₂CH₃), 1.60 (–COOCH₂CH₂CH₂CH₂CH₃), 2.05 (–OH), 3.65 (–COOCH₂), 4.08 (–COOCH₂–). FT-IR (Nicolet 560 FT-IR spectrometer, μm⁻¹): 3530 (–OH), 2800–3000 (C–H), 1732 (ester C = O), 1435–1440 (C–H from –COOCH₂).

2.3. Modification of CaCO₃

Ten grams of nano-CaCO₃ particles were dispersed in 20 g acetone in a glass bottle. After 0.4 g FAS-17 and 0.4 g acidic water (pH 3, adjusted by acetic acid) were charged, the mixture was transferred into a 100 mL glass flask equipped with a mechanical stirrer. After heated to 50 °C, the reaction solution was stirred for additional 2 h. Then the solution was poured into a glass vessel and dried at 60 °C in an oven. After removal the solvents, the modified CaCO₃ particles were obtained as white powder.

2.4. Fabrication of coatings

Five composite coatings were fabricated from the modified CaCO₃ and the polyacrylate at their weight ratios of 9/1, 8/2, 7/3, 6/4 and 5/5 by a simple process. For example, the coating formed at weight ratio of 8/2 is described as follows: 1 g polyacrylate solution (at 50% concentration) and 2 g modified CaCO₃ were added into a glass flask equipped with a mechanical stirrer. After diluted by 1.5 g butyl acetate, the mixture was stirred at 50 °C for 30 min. The mixture was directly coated on glass and copper plates with thickness of 200 μm using an applicator. Then the plates were transferred into an oven and dried at 120 °C for 10 min to complete the drying process. The composite coatings were obtained with thickness less than 200 μm. By the same procedure, modified CaCO₃ based coating and polyacrylate based coating were also formed on the plates.

2.5. Characterization of super hydrophobic coating surfaces

The coating surfaces were imaged by Hitachi-S530 scanning electron microscope (SEM) after the samples were coated with
a thin layer of gold. The composition of the coating surface was analyzed by X-ray photoelectron spectroscopy (XPS, AEM PHI5300, PE) with a sampling depth of 3 nm. Water contact angle measurements were carried out to quantify the degree of hydrophobicity using a contact angle meter (Dataphysics Inc., OCA-20). A water droplet of 5 μL was placed at three different places of the surface under investigation and the average value was taken as the contact angle so as to increase the accuracy. The term sliding angle is defined as the critical angle at which a drop of certain weight spontaneously starts to slide down an inclined surface [18]. Sliding angle measurements of a water

<table>
<thead>
<tr>
<th>Weight ratio of modified CaCO₃ and polyacrylate</th>
<th>Water contact angle (°)</th>
<th>Water sliding angle (°)</th>
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<tbody>
<tr>
<td>1/0</td>
<td>135</td>
<td>4</td>
</tr>
<tr>
<td>9/1</td>
<td>152</td>
<td>–</td>
</tr>
<tr>
<td>8/2</td>
<td>155</td>
<td>2</td>
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<tr>
<td>7/3</td>
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<td>6/4</td>
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<td>5/5</td>
<td>120</td>
<td>40</td>
</tr>
<tr>
<td>0/1</td>
<td>55</td>
<td>&gt;40</td>
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Fig. 1. IR spectra of (a) initial CaCO₃ and (b) modified CaCO₃ by FAS-17.

Fig. 2. SEM images of (a) modified CaCO₃ surface, (b) composite surface formed at weight ratio of 8/2, and (c) composite surface formed at weight ratio of 5/5.
droplet (10 µL) were carried out by using a device fabricated by us, which consisted of one fixed and one moving platforms so as to adjust the angle of inclination. The coated samples were mounted on the movable platform and the sliding angles were measured by using a protractor with an accuracy of ±0.5°. The processes of frost formation on the sample surface were observed directly by an apparatus detailed in our recent article [19].

3. Results and discussion

It has been reported that nano-sized CaCO₃ can be successfully modified by γ-methacryloxypropyltrimethoxysilane due to the existence of reactive surface impurities, such as Ca(OH)₂ [20]. In this paper, we tried to modify nano-sized CaCO₃ by using heptadecafluorodecyl trimethoxysilane (FAS-17). Under the help of acidic water, FAS-17 hydrolyzed and condensed with the surface hydroxyl groups of CaCO₃. The resulting modified CaCO₃ was Soxhlet extracted with xylene for 12 h. The IR spectra of the original and extracted CaCO₃ are shown in Fig. 1. The modified sample possesses two new peaks at 1150 cm⁻¹ (for C–F) and 1240 cm⁻¹ (for Si–O–Si) compared with the original one [21,22], indicating the presence of fluorochains in modified CaCO₃. A coating fabricated from butyl acetate solution of modified CaCO₃ possesses water contact angle of 135° and water sliding angle of 4° (see Table 1). Similar to Yu’s result [20], such high hydrophobicity should be attributed to the surface modification of the particles by FAS-17. However, due to the poor adhesion of inorganic particles, the modified CaCO₃ coating was easily destroyed even by finger touching.

To improve the coating performance, we prepared an ordinary polyacrylate via radical copolymerization of MMA, BA, AA and HEMA, and used it as the binder for modified CaCO₃. The resulting polyacrylate was characterized by GPC, DSC, ¹H NMR and FT-IR with the results shown in the section of materials and methods. Based on modified CaCO₃ and the polymer, a series of composite coatings were fabricated under different weight ratios shown in Table 1 by a simple procedure. The water contact angle and water-sliding angle of the resulting coatings were measured with the results shown in Table 1. The coating formed from polyacrylate alone has a water contact angle of only 55°, indicating a low hydrophobicity. As increasing the content of polyacrylate in the composite coating, the water contact angle increases firstly to the highest value of 155° at the weight ratio of 8/2, and then decreases gradually until 120° is obtained at the weight ratio of 5/5. It is clear that superhydrophobic coatings are obtained at the weight ratios of 9/1 and 8/2. In addition, the water sliding angle changes in accordance with the surface hydrophobicity, i.e. lower water sliding angle is obtained for the surface with higher water contact angle. Therefore the surface properties of the coatings can be easily controlled by the feeding composition of the components. Contrary to modified CaCO₃ coating, the composite coatings adhere tightly to the substrates due to the high adhesion of the polymer.

To get an insight of the surface morphology, the coating surfaces were observed by SEM. Fig. 2 shows the micro- and nano-sized areas of different samples. From Fig. 2(a), there are many ditches on modified CaCO₃ surface, indicating a poor adhesion of the particles. On the nano-sized area, the surface is composed of many nano-sized particles with rather unclear boundary. But from Fig. 2(b) and (c), nearly no defection is found on the composite surfaces formed at weight ratios of 8/2 and 5/5. On the surface formed at weight ratio of 8/2, there are many micro-sized protuberances with each protuberance composed of many nano-sized particles with clear boundary. Similar to the surface of lotus leaf [6], these micro- and nano-sized (a) C1s
(b) Ca2p
(c) F1s
(d) F1s

Fig. 3. XPS spectra of some typical elements: (a–c) are for superhydrophobic surface, and (d) is for modified CaCO₃ surface.
microstructures make the composite surface rather rough and hydrophobic. However, from Fig. 2(c), there are only few nanoparticles on the surface formed at weight ratio of 5/5. This result indicates that the particles are difficult to migrate out at high content of the polymer, therefore decreasing the surface roughness. So the surface microstructures can be controlled by the composition of the two components.

The coating surface was further analyzed by XPS at a depth of 3 nm for analyzing the typical elements and their relative contents. The XPS results of superhydrophobic surface obtained at weight ratio of 8/2 are shown in Fig. 3(a), (b) and (c). From Fig. 3(a), the peaks at 284.8 and 289.9 eV of C 1s are attributed to C–H, and both C–F and C–O [23]. From Fig. 3(b), in the spectra of Ca 2p, the double peaks centered at 347.2 and 350.5 eV represent the spin–orbit doublet of 2p3/2 and 2p1/2, respectively [24]. From Fig. 3(c), the peak at 689.1 eV of F 1s is associated with C–F [21]. The XPS spectra of C 1s, Ca 2p and F 1s indicate that both CaCO₃ and fluoro chains exist at the coating outmost layer. Fig. 3(d) shows the F 1s spectra of modified CaCO₃ surface. The peak intensity of such surface is obviously lower than that of the superhydrophobic surface with their relative fluorine contents at 8.24% and 11.82%, respectively.

For the composite coating, due to the different polarity of the polymer and modified CaCO₃, phase separation took place during the fabricating process. Therefore the particles are forced to accumulate with each other to make fluoro chains gathering at the surface. However, due to the lack of such phase separation, the preferred location of fluoro chains is not noticed for modified CaCO₃ coating. Based on the above results, the superhydrophobicity of the composite coating is attributed to both the surface microstructures and the surface enrichment of fluoroalkyl chains. So the surface structure of superhydrophobic coating can be defined in Fig. 4, in which the micro-sized
Protuberance is composed of many nano-sized particles with the fluoroalkyl chains stretching outside.

To test the dust removability, a glass plate coated with the superhydrophobic coating was placed at a slope angle of 20° and carbon black powder as dirty was deliberately spread on it. If water was dropped to the upper side of the plate, the spherical water droplet rolled quickly to the lower side due to the rather low sliding angle. From Fig. 5, the black powder is removed as the droplet rolling through it. After all the powder being removed by the droplets, a cleaning surface is obtained. Fig. 5(d) indicates that the powder moves to the droplet surface and goes along with the rolling droplet, revealing the similar self-cleaning function of lotus leaf.

In our recent article, the crystal formation process indicated that the frost crystals grew up from water droplet condensed on cold surface [19]. In this paper, we focused on the frost formation on the surfaces with different hydrophobicity. To compare the anti-frosting performance, the processes of frost formation on the surfaces were observed and recorded by using a microscopic image acquisition system with the sampling plate horizontally mounted [19]. Because the images were recorded every 2.5 s at magnifications up to 480 times, it was possible to obtain the initial frosting time from the images. The typical stages during frost formation on various surfaces are shown in Fig. 6. The bare copper surface has a water contact angle of only 64°, on which the initial frost is noticed after only 50 s (see Fig. 6(a)). On the hydrophobic surfaces, spherical droplets are noticed firstly and sometime later the frosts begin to grow at the droplet surface. As the surface water contact angle changed from 120° to 155°, the condensed droplets become larger and the initial frosting time changes from 120 to 150 s. Fig. 7 displays the shapes of water droplets on different surfaces with the bare copper surface covered almost completely by irregular small dots and the hydrophobic surface covered partly by large-sized droplets. Despite of the complicated frost formation process [19], the different anti-frosting performance should be attributed to the different condensation states of water on the surfaces. Due to the different contacting area between the

Fig. 6. Formation of frosts on (a) bare copper surface, (b) hydrophobic surface with contact angle of 120°, and (c) superhydrophobic surfaces with contact angle of 150°. Conditions: temperature −7.2 °C, humidity 55%. The arrow indicating the initial frost.

Fig. 7. Morphology of water droplets condensed on (a) bare copper surface, and (b) hydrophobic surface with water contact angle of 120°.
droplet and the cold surface, both the heat transferring capability and water-cooling rate decrease as larger droplets are formed on the surface. Therefore longer time is required for forming the initial frosts on more hydrophobic surface. This result indicated that superhydrophobic surface is effective in retarding frost formation due to its special surface characters.

The superhydrophobic plate was also mounted vertically on the measuring apparatus and the anti-frosting performance was measured under the same condition. From the results in Fig. 8, nearly no frost is found on the surface even after 600 s testing. Due to a rather small sliding angle, water droplets are difficult to condense on the surface, therefore improving the performance further.

Finally, the stability of the superhydrophobic surface was investigated by freezing–thawing treatment. The superhydrophobic plate was horizontally placed in a refrigerator with the temperature kept at −10 °C until frosts grew up at 5 min. Then it was moved out and stored at ambient environment until the surface was completely dried. After repeating this freezing–thawing process for 10 times, the surface still kept super hydrophobicity, which made the initial frost formed at 140 s. This stable character is important for the surface to achieve practical application. In summary, we described here an easy process for forming superhydrophobic coating. The anti-frosting performance provided by such surface should make the coating suitable for various industrial purposes.

4. Conclusion

Super hydrophobic coating with water contact angle of 155° was prepared from modified CaCO₃ and polyacrylate at their weight ratio of 8/2. The super hydrophobicity can be attributed to both the surface microstructure and the surface enrichment of fluoroalkyl chains. Carbon black power was easily removed from such surface by the rolling water droplet. The formation of frosts on the super hydrophobic surface was greatly retarded compared with that on bare copper surface. The anti-frosting performance was further improved as the coating position changed from horizontal to vertical. The surface kept super hydrophobicity even after freezing–thawing treating for 10 times.

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References