7th International Conference on the Durability of Concrete Structures
20-22 May 2022
University of Jinan, Jinan, Shandong, China

Super-hydrophobic Hybrid Coatings Preparation used by Methyltrithoxysilane (MTES) and Tetraethylorthosilicate(TEOS)

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ABSTRACT

Super-hydrophobic materials, due to their excellent hydrophobic self-cleaning properties, have broad application prospects in aerospace, marine engineering, de-icing and anti-corrosion, etc. In this paper, we prepared super-hydrophobic coatings by simple sol-gel. Methyltriethoxysilane (MTES) and Tetraethylorthosilicate (TEOS) were used as precursors to form rough structures after hydrolytic condensation, and 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FAS) as the surfactant with low surface energy, and systematically studied the best ratio of each component. Hydrophobicity and morphologies of the coating were characterized by water contact angle measurement, scanning electron microscopy (SEM), respectively. Meanwhile, its functional group was characterized by infrared spectrum. Based on a great number of experiments and optimization tests, the resulting hybrid coatings were equipped with fascinating hydrophobicity, which the water contact angle as high as 152°.
Key words: super-hydrophobic coating, sol-gel, wetting

1. INTRODUCTION

Super-hydrophobic coating is a kind of biomimetic material based on the “lotus effect” with a contact angle larger than 150 ° and a roll angle less than 10°[1]. As it possesses excellent characteristics such as self-cleaning, anti-adhesion, anti-corrosion, anti-fog and so on, the preparation of super-hydrophobic coating has aroused great attention between academia and industry. The surface with low surface energy and micro-nano roughness is two essential conditions to achieve superhydrophobicity [2, 3]. Considering the important role of building micro roughness and modifying rough substrates with low-surface energy compounds in the process of preparing super-hydrophobic coatings [4], at present, the artificial super-hydrophobic surfaces mainly lies in two aspects: one is to construct roughness similar to the microstructure of lotus leaf; the other is to modify low-surface energy compounds on the basis of rough substrates. After decades of research, the main methods used to prepare super-hydrophobic materials were as follows: sol-gel [5], template [6], chemical vapor deposition [7], self-assembly [8], etching [9], electrospinning [10] and phase separation [11], etc.

The sol-gel method is widely used because of its low cost, simple process, and being suitable for large-area film formation [12, 13, 14]. With ethyl orthosilicate, ethanol and three different modifiers as raw materials, J Vasiljevic et al [15] prepared hydrophobic and oil-repellent coatings by sol-gel method, with water contact angle of more than 150° and oil contact angle of more than 120°. Rao et al [16]. prepared silica aerosol with superhydrophobic by sol-gel method, and methyltrimethoxysilane, ammonia and methanol were used as the precursor, catalyst and solvent, respectively. It is reported that lower surface energy can be obtained by modifying the surface with a fluorine-containing compound, thereby obtaining a superhydrophobic surface. However, in previous studies, the mutual matching of raw materials still has an insufficient influence on the superhydrophobic properties of the coating film.

In this paper, with MTES and TEOS as precursors, silicone-acrylic emulsion as the crosslinking agent, FAS as surfactant to modify coating with low surface energy compounds, organic and inorganic hybrid super-hydrophobic coating was prepared by means of sol-gel method. The effects of the molar ratio of MTES to TEOS and the amount of silicone-acrylic emulsion and FAS added on the super-hydrophobic properties of the coating were systematically investigated.

2. EXPERIMENTAL

2.1 Raw materials

Both absolute ethyl ethanol and ammonia were analytical grade from Sinopharm Chemical Reagent Co., Ltd. MTES, TEOS and FAS with more than 96% purity were all from Shanghai Macklin Reagent co., Ltd. The Silicon-acrylic emulsion used in this study contained 47% solid content which was purchased from BATF Industrial Co., Ltd.

2.2 Sample preparation

A certain amount of absolute ethyl alcohol, ammonia and silicon-acrylic emulsion were mixed in the flask. The resulting solution was firstly stirred at the speed of 4500r/min for 15min under the water-bath temperature of 60℃. And then the TEOS was added and stirred for another 60min. Subsequently, a mixture of MTES and absolute ethyl alcohol was added drop by drop and stirred at flask for two hours. Finally, organic-inorganic hybrid sol was prepared after adding a certain amount of FAS and stirred for 1 hour. Brush the prepared super-hydrophobic paint on the surface of the glass slide with a brush, and then painted again after drying, superhydrophobic films were achieved after three times.

2.3 Sample characterization

The prepared hybrid sol was brushed on the surface of slide glass to form the coating. The contact angle (CA) test was performed in contact angle instrument (ZhongChen Digital JC2000D3A, China). The surface morphology of the coatings is characterized by scanning electron microscope (QUANA FEG 250, Britain). The chemical component is characterized by Flourier Transformation Infrared Spectroscopy (Micolet 380, America).

3. RESULTS AND DISCUSSION

3.1 Reaction mechanism

The reaction mechanism of super-hydrophobic sol-gel is shown in Fig.1 Under alkali-catalyzed conditions, both MTES and TEOS hydrolyzed in solvent and formed network structures. C_2H_5-O-Si-$(OH)_3$ was synthesized by TEOS poly-condensation independently. With the prolongation of reaction time, larger particles would be synthesized between these condensation products. And the particles with large size will lead to cracking and spalling.. Previous studies demonstrated that the hydrolysis rate of MTES was slower than the TEOS and the hydrolysis product CH3-Si-(OH)3 could react with, the product of TEOS hydrolysis self-condensation polymerization, which could make the hydroxyl group on the surface be replaced by methyl group and inhibited the continuous growth of SiO_2 particles [17]. The SiO2 generated by the above reactions forms the rough structure of coatings, and the introduction of -CH3 on the surface also causes SiO2 particles to have hydrophobic properties. However, inorganic SiO2 particles do not have film forming function, the use of silicone acrylic emulsion encapsulates numerous SiO2 particles, and the inorganic network is dispersed in organic matter, resulting in the formation of an excellent organic and inorganic hybrid film. The use of FAS introduced -CF3 into the original silica sol, according to the surface energy of various functional groups, the order was -CH2- > -CH3 > -CF2- > -CF2H > -CF3. It is obvious from this order that the introduction of -CF3 could significantly reduce the surface energy and optimize the hydrophobic performance.

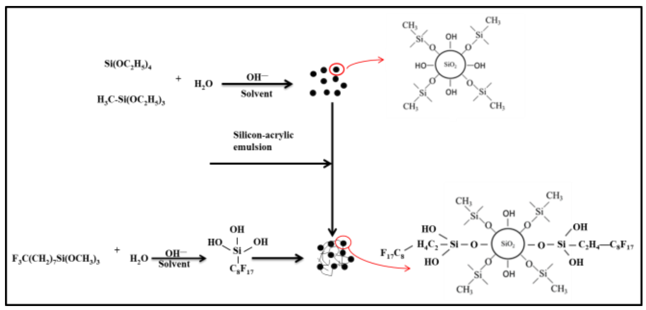

Figure 1. Reaction mechanism of MTES and TEOS

3.2 Effects of silicon-acrylic emulsion on coating properties

In this section, the molar ratio of MTES to TEOS was fixed as 1:2, and FAS was added and accounts for 2% of total moles of MTES and TEOS. The influence of silicon-acrylic emulsion on the hydrophobic performance of hybrid coating is shown in Fig.2.
The contact angle increases first and then decreases with the increase of the silicone-acrylic emulsion. It reaches the maximum when the silicone-acrylic emulsion is added 15% by weight based on the total weight of the emulsion. This is principal because the main function of silicone-acrylic emulsion is to improve the film forming properties of hybrid materials. When the content of silicone-acrylic emulsion is low, a crack is easily produced. And the

water droplets are easily immersed in the substrate through cracks, hence resulting in poor hydrophobic performance. However, when the dosage is too high, the excessive silicone-acrylic resin will be coated on the surface of SiO_2 particles, and the rough surface will be filled up. It can be seen from the two necessary conditions of super-hydrophobic preparation that the hydrophobic performance decreases under these circumstances.

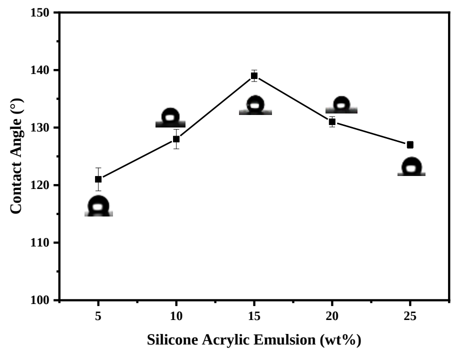

Figure 2. Effects of silicone-acrylic emulsion on water contact angle of coating

Fig.3 (a) and (b) show the infrared spectrum of silicon-acrylic emulsion and organic-inorganic hybrid super-hydrophobic coating, respectively. It can be seen that the C-H and C=O groups are obviously existed at 3000 cm^{-1} and 1730 cm^{-1} in the silicone-acrylic emulsion, respectively. A broad peak appeared at 3435 cm^{-1}, indicating the presence of water molecules (related to structure water and free water), the -OH and Si-OH groups of ethanol on the surface of silica-sol. There is a bending vibration absorption peak of H-O-H at 1650 cm^{-1}, indicating that a small amount of moisture remained in the SiO_2 particles. Two strong peaks appear near 1100 cm^{-1} and 783 cm^{-1}, which are the symmetric stretching vibration peak and the asymmetric stretching vibration peak of Si-O-Si, respectively. Both silicone-acrylic emulsion and silica-sol contain these two peaks.The figure contains characteristic peaks of silicone-acrylic emulsion and silicon-sol, which proves that the combination of silicon-acrylic emulsion and silicon-sol is purely physical, and each of them forms their own network structure respectively.

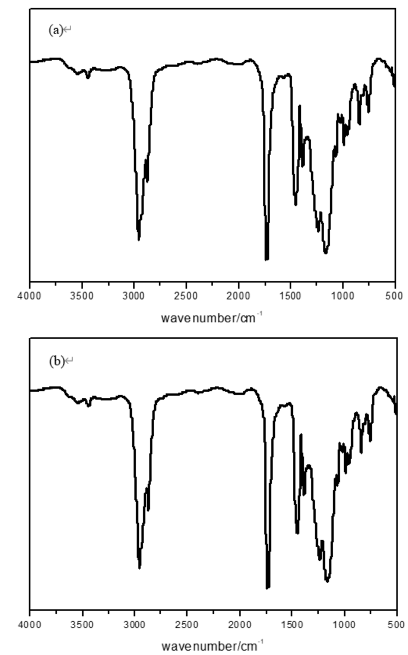

Figure 3. FT-IR spectra of (a) silicone-acrylic emulsion and (b) organic-inorganic hybrid super-hydrophobic coating

3.3 Effects of molar ratio of MTES to TEOS on coating properties

The best dosage of silicon-acrylic emulsion (15 wt%) in the previous section was selected to carry out the experiment in this section. Keeping FAS account for 2% of the total molar numbers of MTES and TEOS, the influence of different molar ratios of MTES to TEOS on the hydrophobic performance of hybrid coatings was discussed.

Fig.4 shows the trends of water contact angle on hybrid coatings under different molar ratios of MTES to TEOS. It can be seen that with the increase of the molar ratios of MTES to TEOS, the contact angle of water droplets on the surface of coatings increase first and decrease subsequently. When n(MTES)/n(TEOS) is 1:2, the contact angle reaches the maximum and the coating is of the best hydrophobic performance. The primary reason for this phenomenon is that TEOS is mainly used to provide SiO_2 to construct the rough structure of the coating surface, and MTES mainly modifies the chemical composition of SiO_2 particles [18]. At lower MTES contents, organic-inorganic hybrid coatings contain a large number of SiO_2 particles covered with hydroxyl groups on the surface, which have extremely strong hydrophilicity, resulting in poor hydrophobic performance. With the continuous increase of MTES content, hydrophobic methyl group was introduced into the surface of SiO_2 particles, and the hydrophobic performance is improved. The continuous increasing content of MTES results in decreasing of surface roughness. And the preparation of super-hydrophobic coatings needs to meet the two conditions of low surface energy and roughness, so the hydrophobic performance decreases under these conditions.

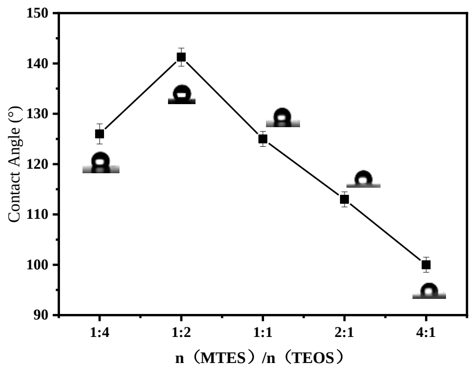

Figure 4. Effects of n(MTES)/n(TEOS) on the water contact angle of coating

3.4 Effects of FAS dosage on coating performances

Based on the above optimum composition ratio of hybrid materials, influences of the different percentages of surfactant FAS on surface wettability were discussed in this section.

From Fig.5, we can draw the conclusions that with the continuous increases of FAS, the values of the water contact angle increase first and then decrease. When the addition amount of FAS accounted for 3% of the total number of MTES and TEOS, the water contact angle of the coatings reached 152°. However, when the addition amount of FAS is 4%, the hydrophobic property decreased and a few cracks appeared on the surface. This is largely due to the chief role of FAS is to reduce the surface energy and meanwhile improve the film-forming property and flexibility of the organic-inorganic hybrid materials. However, the size of the nanoparticles increases with the FAS is added too much, particle aggregation leads to cracks and the hydrophobic property of the coating decreases.

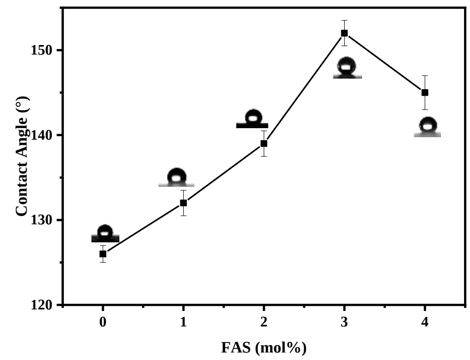

Figure 5. Effects of FAS addition amount on the water contact angle of coating

Fig.6 (a) and (b) are scanning electron microscopic pictures of the hybrid coating when FAS dosage is 3% and 4% of the total molar number of MTES and TEOS, respectively. From Fig.6 (a), it can be seen that inorganic SiO_2 particles diameter are smaller and form hybrid coating by compounding with organic polymers, but still retain the rough structure of inorganic SiO_2 nanoparticles, so the hydrophobicity is better. In contrast, as shown in Fig.6 (b), when FAS content is too high, the size of SiO_2 particle increases, aggregation occurs between particles, micro-cracks appear on the surface of the coating and hydrophobic properties are degraded.

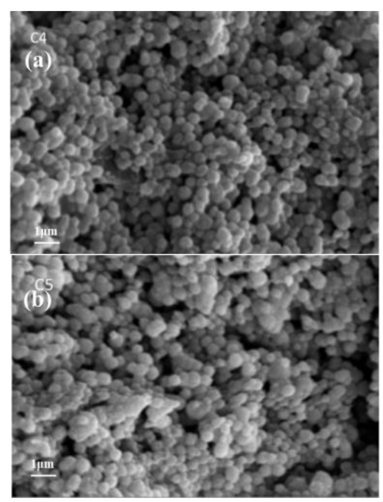

Figure 6. SEM of hybrid coating made from (a) content of FAS was 3% (b) content of FAS was 4%

4 Conclusions

The super-hydrophobic coatings were prepared by a simple sol-gel process without special instruments and equipment. Under alkaline conditions, MTES and TEOS were hydrolyzed and condensed to form SiO_2 particles covered with methyl groups. Silicon-acrylic emulsion was added to the compound with inorganic SiO_2 network to improve the film-forming performance. The addition of FAS reduced the surface energy and improved the hydrophobic property of the organic-inorganic hybrid coatings. By optimizing the experimental parameters, we obtained the best formulation of this type of superhydrophobic coating, that is, when the content of the silicone-acrylic emulsion was 15% of the total weight, the molar ratio of MTES to TEOS was 1:2 and the dosage of FAS was 3% of the total number of moles, the final coating's contact angle as high as 152°, has excellent hydrophobic performance.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 52172021), National Natural Science Foundation of China-Shandong Joint Fund Key Project (No. U1806222) , Natural Science Foundation of Shandong Province (ZR2021ME123), Key Laboratory of Advanced Civil Engineering Materials (Tongji University), Ministry of Education (202001), the Taishan Scholars Program, Case-by-Case Project for Top Outstanding Talents of Jinan, Science and Technology Project of University of Jinan (XKY2003).

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