A facile method of fabricating mechanical durable anti-icing coatings based on CeO_2 microparticles

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Abstract. Compromising between hydrophobicity and mechanical durability may be a feasible approach to fabricating usable anti-icing coatings. This work improves the contact angle of current commercial anti-icing coatings applied to wind turbine blades dramatically and keeps relatively high mechanical durability. CeO_2 microparticles and diluent were mixed with fluorocarbon resin to fabricate high hydrophobic coatings on the glass fiber reinforced epoxy composite substrates. The proportion of CeO_2 microparticles and diluent influences the contact angles significantly. The optimum mass ratio of fluorocarbon resin to CeO_2 microparticles to diluent is 1:1.5:1, which leads to the highest contact angle close to 140°. The microscopy analysis shows that the CeO_2 microparticles form nano/microscale hierarchical structure on the surface of the coatings.

1. Introduction

Superhydrophobic surfaces with the water contact angle higher than 150° and the sliding angle less than 10° have attracted much attention in the past ten years [1-3]. There are many superhydrophobic surfaces in nature, and the best well-known example is the lotus leaf with the water contact angle of up to 160° [4, 5]. The SEM pictures of the lotus surface showed that the combination of micrometer/ nanometer-scale roughness and epicuticular wax led to the superhydrophobic properties [6].

Superhydrophobic surfaces can be used in a variety of fields such as anti-icing, waterproof, self-cleaning, etc. Fabricating superhydrophobic surfaces includes two strategies: the one is constructing nano/microscale hierarchical structure on the intrinsic hydrophobic substrate, the other is modifying rough surface microstructures using low surface energy materials [7-9]. The common methods include template method [10], etching method [11], brush-coating [12], electrospinning technique [13], sol-gel method [14], layer-layer assembly [15-17], electrochemical deposition [2, 18, 19] etc.

However, most methods either have complicated processes or need expensive materials and experimental apparatus [20]. Thus, this is not conducive to large-scale production. Besides, for hydrophobic coatings, their mechanical durability is usually very poor and easily abraded by external forces [21]. Recent studies show that rare-earth metal oxide has not only good hydrophobicity but also

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durability properties [22]. CeO_2 is one kind of rare-earth metal oxide and has never been utilized to fabricate anti-icing coatings. Within, we report a simple method to fabricate a mechanical durable anti-icing coating by mixing CeO_2 microparticles and diluent with fluorocarbon resin. This method is easily controlled, and the raw materials are cheap [12, 20]. Furthermore, the coatings have good mechanical durability and can be cured at room temperature.

2. Experimental

2.1. Materials and method

Anti-icing coatings were made from the mixture of fluorocarbon resin (Obtained from Zhuzhou Times New Material Technology CO., LTD, China) with CeO_2 microparticles (obtained from Ganzhou Goring High-tech material Corporation Limited, China) and diluent. Diluent is the mixture of dimethylbenzene and butyl acetate (the mass ratio of dimethylbenzene to butyl acetate is 6:4). The curing agent is isocyanate (the ratio of resin to curing agent is 5:1). The diameter of CeO_2 microparticles is 10 μm.

Took 10 g fluorocarbon resin in the beaker, then diluent, CeO_2 microparticles and isocyanate were added to it in order. Finally, the mixture was homogeneously mixed by an electromagnetic stirrer. Took a certain amount of the coatings to brush on the composite material substrates and cured at room temperature.

We mainly studied the effects of the amount of CeO_2 microparticles and diluent on the hydrophobic properties of the coatings. Firstly, we studied the effects of diluent. The experimental formulations are shown in table 1.

Table 1. The experimental formulations of different amount of the diluent.

No.	Fluorocarbon resin (g)	Isocyanate (g)	Diluent (g)	CeO_2 microparticles (g)
A1	10	2	2.5	5
A2	10	2	5	5
A3	10	2	10	5
A4	10	2	20	5
A5	10	2	30	5
A6	10	2	40	5
A7	10	2	50	5

After finding the optimal amount of diluent based on the influence rules of which on the hydrophobic properties of the coatings, we changed the amount of CeO_2 microparticles to study the effects on the hydrophobicity of the coatings. The experimental formulations are shown in table 2.

Table 2. The experimental formulations of different amount of CeO_2microparticles.

No.	Fluorocarbon resin (g)	Isocyanate (g)	Diluent (g)	CeO_2 microparticles (g)
B1	10	2	10	1
B2	10	2	10	3
B3	10	2	10	5
B4	10	2	10	8
B5	10	2	10	10
B6	10	2	10	15
B7	10	2	10	20

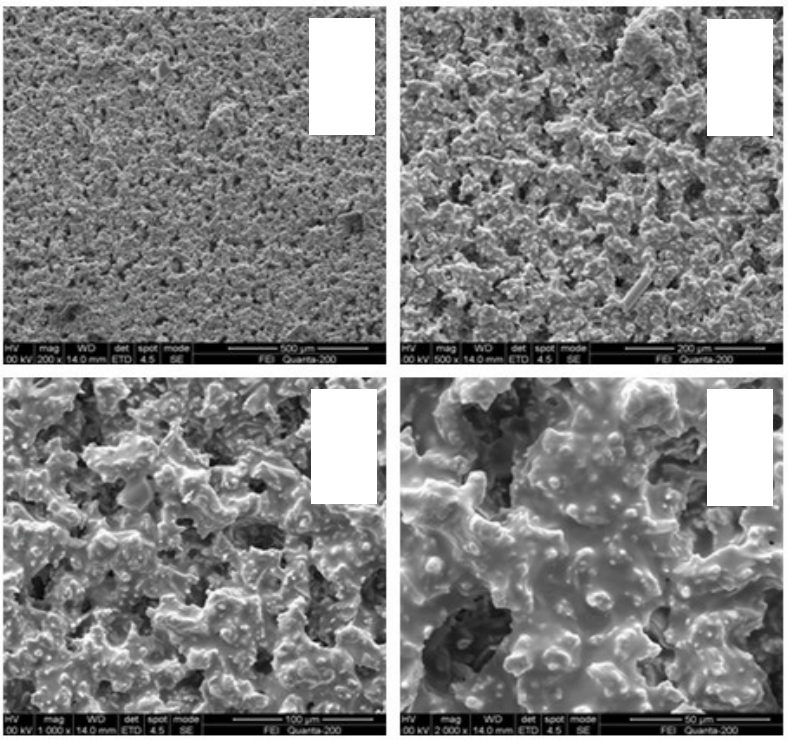

Figure 1. SEM pictures of anti-icing coatings whose mass ratio of fluorocarbon resin to CeO_2 microparticles to diluent was 1:0.5:0.5. The scales of SEM pictures were 500 μm, 200 μm, 100 μm and 50 μm for a, b, c and d, respectively.

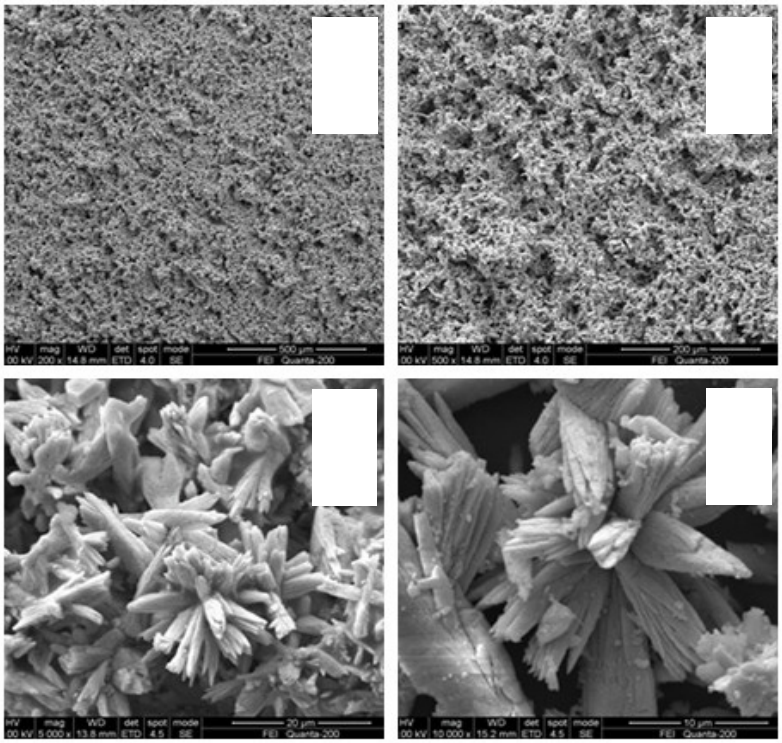

Figure 2. SEM pictures of anti-icing coatings whose mass ratio of fluorocarbon resin to CeO_2 microparticles to diluent was 1:0.5:2. The scales of SEM pictures were 500 μm, 200 μm, 100 μm and 50 μm for a, b, c and d, respectively.

2.2. Characterization

The contact angle was measured by Standard Contact Angle Meter SL-200B (SHANGHAI SOLON INFORMATION TECHNOLOGY CO., LTD, China) in this work. A pipette was used to inject a water-drop on the surfaces of the coatings and the droplet formed a contact angle with the solid surface. The instrument was focalized to make the image of droplet showing on the screen clearly. After measuring the contact angle, the results were corrected by Elliptic Curve Method. Five different points of every sample were measured, and their averages were taken as the final results.

A scanning electron microscopy (SEM) of Quanta-200 (FEI Company, USA) was utilized to verify the nano/microscale hierarchical structures of the coatings. The samples were gold-sputtered before scanning. And then they were fixed on the sample plate to take photos under the vacuum condition.

3. Results and discussion

3.1. Surface morphology of coatings

Figures 1 and 2 display the results of SEM pictures of the obtained anti-icing coatings (the scales of SEM pictures are 500 μm, 200 μm, 100 μm and 50 μm, respectively). The mass ratio of fluorocarbon resin to CeO_2 microparticles to diluents was 1:0.5:0.5. Figure 1 displays that the surface presented to be porous and the diameter of the micropore was about 10μm. The main substance of the surface was the cured rock-shaped resin and some bulges comprised of CeO_2 microparticles were distributed on it. But the whole regularity was not good. The possible reason was the amount of resin was still large, and the CeO_2 microparticles were resin-clad.

In figure 2, the amount of diluent increased. The mass ratio of fluorocarbon resin to CeO_2 microparticles to diluent was 1:0.5:2. From the pictures, the surface still presented to be porous. An amount of chrysanthemum-shaped bulges were distributed on it. Nanoscale lamellar structures appeared on the tops of the chrysanthemum-shaped bulges. The combination of them constructed nano/microscale hierarchical structure.

From figures 1 and 2, the porous structure of the coatings surface and the bulges comprised of CeO_2 microparticles became clearer and clearer with the increase of the amount of diluent. When diluent increased, the resin in per unit volume of the coatings became less, the CeO_2 microparticles would not be resin-clad and could well subside on the surface to comprise nano/microscale hierarchical structure.

From figures 1 and 2, we also found that the CeO_2 microparticles had different effects on the hydrophobicity of the coatings under the condition of two kinds of amounts of diluent. So we fixed the mass ratio of fluorocarbon resin to diluent to be 1:2, then changed the amount of CeO_2 microparticles and observed the coatings microstructure. Under this condition, figure 3 shows the SEM pictures of anti-icing coatings whose mass ratio of fluorocarbon resin to CeO_2 microparticles was 1:0.3 and 1:1, respectively.

Figure 3 shows that the microstructures of these two samples were very similar. They both presented to be rough and had flower-shaped bulges comprised of CeO_2 microparticles. The results demonstrate that the change of the amount of CeO_2 microparticles has little effects on the coatings microstructure under this condition.

3.2. Hydrophobic properties of coatings

The contact angles (CA) of the anti-icing coatings are shown in tables 3 and 4.The results in table 3 indicate the influence rules of diluent on the hydrophobicity of the coatings. It shows that when the mass ratio of fluorocarbon resin to diluent was bigger than 1:1, the CA was less than 70°. While the mass ratio was 1:1, the CA significantly increased to 137.88° which indicated the coatings already had good hydrophobic properties. It is because when the ratio was bigger than 1:1, the surface of the substrate was mainly covered by resin, so the CeO_2 microparticles could not construct rough surface. But when the mass ratio was less than 1:1, the amount of resin decreased. So the sedimentary CeO_2 microparticles which have hydrophobic properties formed the bulges and constructed the porous

chrysanthemum-shaped microstructure (shown in figure 2). As a result, the CA increased significantly. From table 3 we also found that when the mass ratio of fluorocarbon resin to diluent was less than 1:1, keeping adding diluent had little effects on the CA.

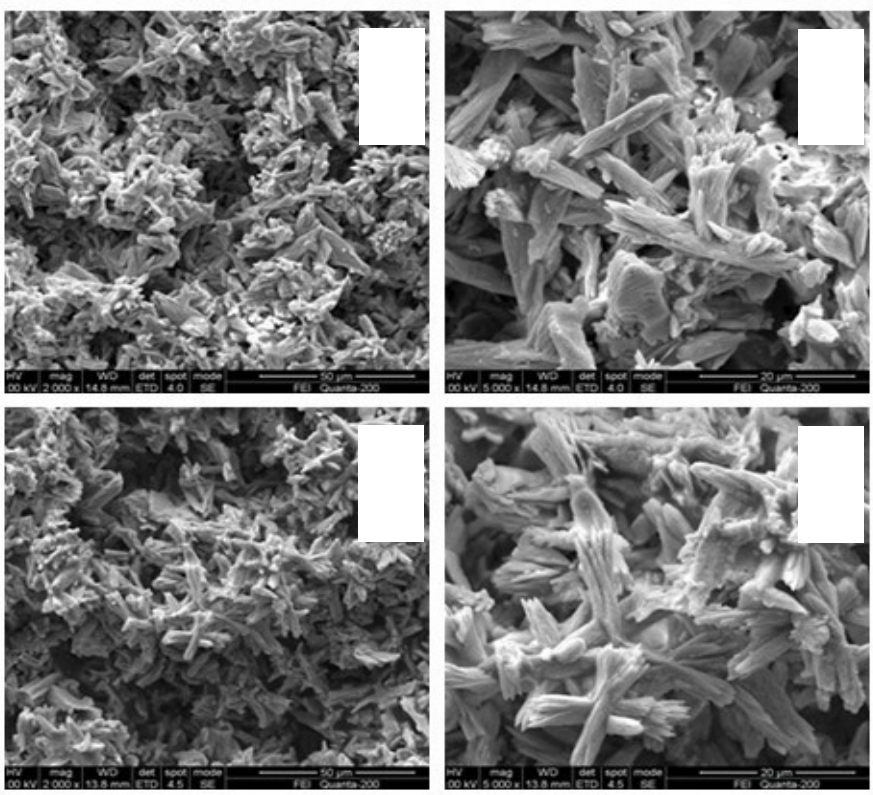

Figure 3. SEM pictures of anti-icing coatings. For a and b, the mass ratio of fluorocarbon resin to CeO_2 microparticles to diluent was 1:0.3:2. For c and d, the mass ratio was 1:1:2. The scales of SEM pictures were 50 μm, 20 μm, 50 μm and 20 μm for a, b, c and d, respectively.

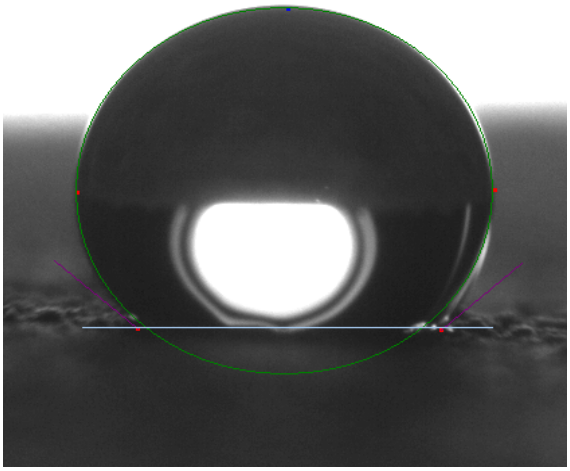

Figure 4. Water drop deposited on the anti-icing coatings surface: CA is 139.93.

Table 4 displays the influence rules of CeO_2 microparticles on hydrophobic properties of the coatings under the condition of high diluents concentration. The highest CA in table 4 is close to 140° of which the mass ratio of fluorocarbon resin to CeO_2 microparticles to diluent is 1:1.5:1(showed in figure 4). The influence of CeO_2 microparticles on the hydrophobic properties is not significant. In fact, when the amount of diluent is large, the CeO_2 microparticles can be easily homogenized in the

coatings to construct nano/microscale hierarchical structure, so changing the amount of CeO_2 microparticles has little effects. Also, the CA became less with the decrease of CeO_2 microparticles. This is because when the particles decrease, there are fewer bulges on the coatings surface to construct nano/microscale hierarchical structure.

Table 3. Contact angles of anti-icing coatings (the mass ratio of fluorocarbon resin to CeO_2 microparticles is 1:0.5).

No.	Mass ratio of resin to diluent	CA (°)
A1	1 : 0.25	69.03
A2	1 : 0.5	65.40
A3	1 : 1	137.88
A4	1 : 2	136.45
A5	1 : 3	134.19
A6	1 : 4	138.62
A7	1 : 5	133.06

Table 4. Contact angles of anti-icing coatings (the mass ratio of fluorocarbon resin to diluent is 1:1).

No.	Mass ratio of resin to CeO_2 microparticles	CA（°）
B1	1 : 0.1	130.71
B2	1 : 0.3	131.93
B3	1 : 0.5	134.52
B4	1 : 0.7	128.11
B5	1 : 1	131.91
B6	1 : 1.5	139.93
B7	1 : 2	138.82

Recently, contact angles of most commercial anti-icing coatings for wind turbine blades are about 110° and these coatings are usually very weak to resist mechanical contact. In this work, we obtained coatings of which the highest water contact angle was close to 140°. Besides, these coatings also had good mechanical durability in theory.

4. Conclusions

This work presented a facile method of fabricating mechanical durable anti-icing coatings based on CeO_2 microparticles that could be cured at room temperature. The SEM pictures indicate that the CeO_2 microparticles construct nano/microscale hierarchical structure on the surface of the coatings. The optimum mass ratio of fluorocarbon resin to CeO_2 microparticles to diluent is 1:1.5:1, which leads to the highest contact angle close to 140°, about 30° higher than commercial anti-icing coatings. Furthermore, these coatings can well resist mechanical contact theoretically. This method is simple and conducive to large-scale production. It will promote the hydrophobic surfaces to practical application in the future

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