Effect of perfluoropolyether and the micro nano structure of ZnO on anti icing performance of fluorinated organic superhydrophobicity coatings on wind turbine blade surface

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Abstract

The ice coating on the blade surface of wind turbine in winter seriously affects the operation safety and power generation efficiency of wind turbine, and anti icing and deicing is an urgent technical problem. In this paper, a super-hydrophobic anti-icing coating was prepared by fluorination modification, and the effect of the addition of perfluoropolyether (PFPE) and ZnO on the performance of the coating was studied. The research results show that the addition of PFPE reduces the surface energy of the coating from 18.12 mJ m⁻² at 0% to 13.22 mJ m⁻² at 15%. The surface free energy has a linear relationship with the binding force of icing. With the increase of the amount of PFPE, the contact angle of the coating increases, the sliding angle decreases, and the delayed icing performance improves. When the amount of PFPE reaches 15%, the contact angle reaches the highest value of 158°, and the sliding angle is 2°; adding PFPE coating, the freezing delay time can reach 107.1 s. The addition of PFPE can effectively reduce the icing strength, and the icing bonding force of the coating is reduced to 0.59 N at 15%. The addition of a amount of ZnO can greatly change the microstructure of the coating surface, thereby changing its superhydrophobicity. The fluorinated superhydrophobicity coating modified by the addition and removal of ZnO has obvious anti-icing performance. The 6 wt% sample has the best delayed icing energy.

1. Introduction

The icing on wind turbine blades in winter will not only cause measurement errors of wind speed and wind direction, affecting the yaw and power control of wind turbines, but also can change the blade airfoil and surface roughness, affecting aerodynamic characteristics and power generation output [1]. Large-scale shutdowns due to icing of wind turbines have caused huge power loss each year. Therefore, anti-icing and deicing on the surface of wind turbine blades is an urgent technical problem in the field of wind power.

The anti-icing and de-icing performance of super-hydrophobic coating materials is one of the hotspots of current research [2]. The super-hydrophobicity of the coating makes it difficult for water droplets to stay and accumulate on the surface of the coating. The extremely high contact angle and extremely low sliding angle will reduce the water droplets collecting on the blades before icing; on the one hand, the surface energy is considered to be one of the important factors affecting the anti-icing performance. By changing the ratio of low surface energy and high surface energy nanoparticles while maintaining the total amount of them, Wu et al [3] prepared the surface microscopic characteristics, verifying that the surface morphology and surface energy of the superhydrophobic coating play an important role in the adhesion of ice.

On the other hand, the micro-nano structure of the coating surface structure can further improve the hydrophobicity of the coating. Surface wettability is considered to be one of the important factors affecting anti-icing performance. Kreder et al [4] also believed that only when the contact angle is hysteresis, there will be a...
negative linear relationship between ice adhesion and apparent contact angle. Liu et al. [5] injected polytetrafluoroethylene (PTFE)-polyvinylidene fluoride (PVDF) composite membrane, three slippery liquid-infused porous surfaces (SLIPS) are obtained, which transforms the performance of the composite membrane from super-hydrophobicity to smoothness. Their ice adhesion strength is less than 20 kPa, especially the PFPE infusion surface value is 13.9 kPa, showing excellent ice resistance. Nguyen et al. [6] have studied ice-repellent and transparent surfaces based on the unique structure of coating materials. Paraffin wax was selected as the coating material because of its low thermal conductivity, easy coating, and original water resistance. The countless air masses trapped in the nanostructure also help delay heat transfer, leading to an increase in the freezing time of attached water droplets. It shows outstanding performance in terms of adhesion strength, freezing time and freezing rain sustainability.

The main factors restricting the development of super-hydrophobic coating anti-icing technology are that the complex icing mechanism under the influence of different environmental conditions and water ice complex factors [7, 8]. The influence of the special material and structural characteristics of super-hydrophobic coatings on the complex dynamics of icing [9, 10]. The influence of coating surface free energy and micro-nano structural characteristics on the binding force of icing [11–13]. In this paper, new hydrophobic materials are used to control the free energy of the coating surface, adding or reduce nanoparticles is used to control the micro-nano structure of the coating surface, and the effect of the surface characteristics of the nano-superhydrophobic coating on the anti-icing performance is studied.

2. Experimental method

2.1. Coating preparation
Dilute a amount (0, 0.1 g, 0.2 g, 0.3 g, 0.4 g) of PFPE by adding to 10 ml of deionized water, and add 40g of laboratory-made organic paint to the diluted PFPE, Disperse ultrasonically for 15 min, then stir with a magnetic stirrer for 10 min to obtain a fluorinated organic coating. Then add 2 g ZnO powder to the organic coating and ultrasonically disperse it for 15 min, and stir with a magnetic stirrer at 1000 rpm for 10 min to obtain a nano organic composite anti-icing solution. Spray the solution on glass, and place the sample in a drying box at the temperature of 80 °C for 4 h. Put the dried sample in acetic acid solution for acidification, and then dry the sample to obtain the nano organic composite anti-icing coating. The physical diagrams of the heating magnetic stirrer and ultrasonic cleaner are shown in figures 1 and 2.

2.2. Testing method
The coating samples A1 to A5 with different amount of PFPE and the samples C0 to C5 with different amount of ZnO were placed in a self-made icing test platform for an anti-icing performance test. The experimental
temperature of the sample was selected at $-5^\circ C$, $-10^\circ C$ and $-15^\circ C$. During the experiment, the freezing time of water droplets at room temperature on the sample surface was observed to test the anti-icing ability. Repeat the test 5 times, and take the average of the effective results as the final test result.

The static contact angle tester (JC2000D7M) is used to measure the water contact angle (WCA) and water sliding angle (WSA) of the droplets on the coating surface. The test environment should have a relatively stable temperature and humidity. The test drops are 10 $\mu$L deionized water droplets, which are dripped at 5 different positions on the sample coating with a syringe. The sample needs to be tilted at an angle that the water droplets just started to slide during the water sliding angle (WSA) test. Repeat the test 5 times, and take the average of the effective results as the final test result.

The icing test was carried out with a self-made modified freezer. Add water through the nozzle and record the whole process of icing with the camera. The icing time, ice adhesion size, and the ice weight of different samples under the same conditions were recorded. The schematic diagram of the icing test platform is shown in figure 3.

The shear force deicing test is used to test the adhesion of the icing surface, that is, using external force to shear and fall off the ice from the surface of the sample, and recording the value of the detachment displayed by the electronic dynamometer, which is the icing adhesion [14].

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Figure 2. MMCS-900 physical image of ultrasonic cleaner.

Figure 3. Schematic diagram of icing test platform.
3. Results and analysis

3.1. The result of the effect of PFPE addition to the superhydrophobic properties of the coating.

Figure 4 shows the superhydrophobic properties of the coating with different PFPE addition. It can be seen from figure 4 that as the content of PFPE continues to increase, the contact angle of the coating also increases, reaching the highest value of 158° at 15%, and then there will be a slight decrease. The sliding angle of the coating generally decreases with the increase of the content of PFPE. It reaches about 2° at 15% addition amount, which is obviously negatively correlated, but has a turning point at the 15% of PFPE content. This is because when the content of PFPE reaches a certain proportion, its grafting of the polymerization with epoxy resin saturates. When the content continues to increase, the fluorination modification effect does not change significantly, and excessive PFPE remains has a certain side effect on the superhydrophobic of the entire coating, so the contact angle is maintained at about 158°.

3.2. The effect of PFPE addition to the anti-icing performance of the coating

Table 1 shows the results of the icing test on the surface of coatings with different content of PFPE under the temperature of $-10$ °C. It can be found that the sample that has PFPE content has the ability to delay the icing time, and has a positive correlation to the time. The maximum time delay is 107.1 s (compared with 0% PFPE content), and when the PFPE content reaches 20%, the freezing time of the coating surface respectively reduced 5.3 s and 9.3 s compared with the 15% PFPE content, which showed that its ability of delaying icing time decreased.

Figure 5 shows the freezing duration of the PFPE coating at different temperatures. It can be seen that the freezing time of the same coating decreases as the freezing temperature decreases. At the same freezing temperature, the freezing time of the coating is generally positively increased with the increase in the PFPE content, and reached maxima at 15% PFPE content. Specifically saying, A1 (0% PFPE content) < A2 (5% PFPE content) < A5 (20% PFPE content) < A3 (10% PFPE content) < A4 (15% PFPE content). Comprehensively, it shows that the addition of PFPE to the coating greatly influences the delay of icing time, and can effectively improve the superhydrophobic of the coating. 15% PFPE content has the overall best performance.

Table 1. Time table of $-10$ °C sample freezing.

| Sample label | Start testing (s) | Start to freeze (s) | Completely frozen (s) |
|--------------|-------------------|---------------------|-----------------------|
| A1 (0%)      | 0                 | 620.2               | 631.5                 |
| A2 (5%)      | 0                 | 674.8               | 689.7                 |
| A3 (10%)     | 0                 | 692.3               | 713.1                 |
| A4 (15%)     | 0                 | 716.1               | 738.6                 |
| A5 (20%)     | 0                 | 710.8               | 729.3                 |
3.3. The effect of PFPE content to the icing adhesion of the coating

The icing adhesion is also an important indicator to analyze the anti-icing performance of the coating. Figure 6 shows the experimental results of the icing adhesion of the coating with different PFPE content. It can be seen from figure 6 that the addition of PFPE can reduce the icing adhesion of the coating. Under the same surface area, the coating without PFPE (A1) content has a higher icing adhesion strength of 1.36 N. When the PFPE content reaches 10% and 15%, the icing adhesion of the coating could reach down to 0.59 N. It can be seen that an appropriate amount of PFPE content can reduce the adhesion strength to a certain extent, making the ice coating easier to fall off.

The calculation formula of work to overcome the adhesion of ice surface is as formula (1).

\[ W = \frac{2\pi R^2 h (\gamma_{SL} - \gamma_{SA})}{P} = -2\pi R^2 h \gamma_{LA} \cos \theta_i / P \]  

(1)

There are many and complex factors that affect ice adhesion. Analyze the formula (1) in combination with the geometric parameter diagram of the force analysis. In figure 7, assuming that the ice layer is the hemisphere above the substrate, \( R_1 \) and \( R_2 \) are partial radii, \( H \) is the distance from the substrate to the ice peak, \( \theta \) is the contact angle, \( R \) is the radius of the droplet contact area, and \( \theta_i \) is the intrinsic contact angle, \( \gamma_{SL}, \gamma_{SA}, \gamma_{LA} \) represent the surface tension between solid-liquid, solid-gas, and gas-liquid. It can be analyzed from the formula that the icing is not only closely related to the contact angle, but also related to the contact form of the substrate. Therefore, the two work synergistically and promote each other, which can greatly reduce the adhesion of icing, so as to achieve a hydrophobic effect.

Figure 5. The relationship between freezing duration and temperature of different samples.

Figure 6. Schematic diagram of icing adhesion of different PFPE content.
4. The influence of ZnO powder on the superhydrophobic of the coating

4.1. The addition and removal of ZnO powder creates a micro-nano rough surface of the coating.
Add 0%, 2%, 4%, 6%, 8% and 10% mass ratio of ZnO nano-powder to the fluorinated superhydrophobic coating respectively, and put the prepared coating in a 5% wt butyl acetic acid solution for 5 min to do a powder removal. Take out the sample and dry it in a thermostat at 80 °C for 2 h, and then get the prepared coating samples as C0, C1, C2, C3, C4 and C5. The micro-nano structure of the coating surface is controlled by adding and removing different amounts of ZnO.

Coatings with different mass fractions of ZnO added and removed show different superhydrophobic. The corresponding contact angles and sliding angles are shown in figure 8. It can be seen from figure 8 that as the content of ZnO increases to 6%, the hydrophobic angle of the coating continuously increases, and could reach up to 158.8°. The sliding angle decreases, and could reach down to 2.6°. When the ZnO content increases to 10%, the hydrophobicity becomes stable and then decreases.

Due to the size effect, the gap between the conduction band and the valence band is increased, and the oxidation resistance and abrasion resistance are strong. Perform multiple icing/de-icing experiments on C0 and C3 to test their wear resistance. The metallographic inspection photos of coatings with different ZnO content are shown in the figure 9.

After 50 icing/de-icing cycles, C0 (0%ZnO) has been severely worn, while C3 (6% ZnO) still maintains a good shape. It can be seen that ZnO can increase the wear resistance of the coating, and the super-hydrophobic state can be maintained for a longer time.

4.2. The influence of ZnO addition and removal on the anti-icing performance of the coating
The freezing time-temperature plot of different ZnO addition and removal is shown in figure 10. It can be seen from figure 10 that the fluorinated superhydrophobicity coating modified by ZnO addition and removal has obvious delaying icing time performance. The icing time of sample C0 (without ZnO addition and removal) is
the shortest, while the sample C3 (6 wt%) and C4 (8 wt%) has the best performance in delaying icing time, and also has the longest freezing time under different temperatures. But when the ZnO content continues to increase to 10 wt% (sample C5), the performance dropped sharply, and the icing delay effect basically disappears (nearly equals to sample C0).

Through testing the shear stress of deicing under the same surface area, it can show the icing surface adhesion. Figure 11 is a comparison diagram of the icing adhesion of the coating with different amount of ZnO addition and removal. The sample C0 exhibits relatively high icing adhesion. By comparison, the icing adhesion of sample C3 and C4 is greatly reduced, showing that an appropriate amount of ZnO addition and removal can reduce the strength of ice coating to a certain extent, making the ice coating easier to fall off.

The SEM picture of the micro morphology of the coating with different amount of ZnO content is shown in figure 12. It can be seen from figure 12 that with the increase of the ZnO content, the micro morphology of the coating has a certain change. It can be seen from sample C0 that the PTFE particles on the surface of the sample are evenly distributed. With a small amount (2%) of ZnO addition and removal, the micro morphology of the sample is close to sample C0, but the surface morphology is more complicated than sample C0. With the increase of the ZnO content, there shows obvious gaps on the surface, and the particles are arranged in a clustered structure. Also, there are more obvious particle removal traces between PFPE particles and more gaps and holes on the surface, indicating that the complexity of surface morphology has increased (figures 12(c), (d)). An excessive addition of ZnO (10%) in sample C5 will cause large-scale shedding voids on the surface, with an increase of the number of holes (figure 12(f)). Therefore, the addition and removal of a certain amount of ZnO can modify the microstructure of the coating surface and improve the anti-icing performance of the coating, but excessive addition will also cause the appearance of large pores and gaps and destroy the Cassie-Baxter State [15, 16] constructed by the micro-nano structure, resulting in a decrease in hydrophobic anti-icing performance.
5. Conclusion

(1) With the increase of the amount of PFPE addition, the contact angle of the coating increases, and the sliding angle decreases. At 15% of PFPE content, the contact angle reaches the highest value of 158°, and the sliding angle is 3°. With further increase of the PFPE content, the superhydrophobic performance decreases.

(2) The addition of PFPE has a significant effect on the coating’s freezing time. With the increase in the PFPE content, the icing time increases. The freezing time has the relationship of $A_1$ (0% PFPE content) < $A_2$ (5% PFPE content) < $A_5$ (20% PFPE content) < $A_3$ (10% PFPE content) < $A_4$ (15% PFPE content). Compared with 0% PFPE content, the icing time can reach up to 107.1 s when the sample has 15% PFPE content.
Moreover, the addition of PFPE can effectively reduce the strength of the ice coating, making the ice coating easier to fall off. At $-10^\circ C$, the ice bonding force of the coating without adding PFPE is 1.36 N, while the ice bonding force of the coating is greatly reduced to 0.59 N with 15% PFPE content.

(3) By observing the microscopic morphology and roughness of the sample, it is shown that the addition and removal of a certain amount of ZnO can greatly change the microstructure of the coating surface, thereby changing its superhydrophobicity. The fluorinated superhydrophobic coating modified by ZnO addition and removal has obvious anti-icing properties. The 6 wt% content sample has the best performance, and has the longest icing time under different low temperatures. But when the content continues to increase to 10 wt%, the delaying effect basically disappears.

(4) The adhesion of the icing surface was measured through the shear force deicing test. An appropriate amount of ZnO addition and removal can reduce the strength of the icing to a certain extent, making the ice easier to fall off. The analysis believes that the micro-nano structure of different surfaces will cause the material to produce different icing adhesion, and the appropriate micro-nano structure can better reduce the icing adhesion and make it easier to fall off.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

The authors declare that they have no conflicts of interest to report regarding the present study.

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