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A Study on Wettability and Tribological Properties of Polytetrafluoroethylene and Perfluoroalkyl Vinyl Composite Coatings Polytetrafluoroethylene and Perfluoroalkyl Ethylene Composite Coatings

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Abstract: Fluoropolymers have garnered increasing attention due to their exceptional chemical stability and physical properties. This study prepared composite coatings of polytetrafluoroethylene (PTFE) and perfluoroalkoxy polymer (PFA) with varying ratios using the solution blending method and systematically evaluated their wettability and tribological properties. By adjusting the ratio of PTFE to PFA, the wettability and tribological performance of the composite coatings can be effectively controlled to achieve an optimal balance of friction reduction and wear resistance. The results showed that the wettability of the composite coatings varied significantly with the composition ratio. Initially, increasing the PFA content enhanced the surface roughness and significantly raised the contact angle to 135°. However, excessive PFA content reduced the contact angle. Additionally, the incorporation of PFA improved adhesion between the coating and substrate. When it slightly increased the friction coefficient, it significantly enhanced the wear resistance of the composite coatings. The optimized composite coating exhibited the best overall performance, with a contact angle of 138°, a friction coefficient of approximately 0.23, and a wear rate as low as 2.07×10^{-6} mm^3/Nm. Through this component optimization design, the PTFE/PFA composite coatings demonstrated excellent tribological and wettability characteristics, holding great potential for widespread application in energy equipment, aerospace and advanced manufacturing industries.

1. Introduction

Polytetrafluoroethylene (PTFE) and Perfluoroalkoxy polymers (PFA), as representative fluoropolymers, have been widely used in various fields due to their unique chemical stability and excellent physical properties [1-3]. PTFE, often referred to as the “king of plastics”, due to its unique chemical structure and high fluorine content, exhibits several remarkable characteristics, including an extremely low coefficient of friction, outstanding chemical resistance and exceptional hydrophobicity. Studies have shown that PTFE has a surface energy of only 18 mN/m, one of the lowest among common solid materials. Furthermore, PTFE retains its physical properties over a broad temperature range, from -200 ℃ to 260 ℃, making it extensively utilized in aerospace, chemical corrosion resistance and mechanical sealing applications [4-5]. However, PTFE also has notable drawbacks. Its mechanical strength is relatively low, especially its poor wear resistance, which limits its use in high-load and high-friction environments. To overcome these shortcomings, researchers have attempted to enhance PTFE's properties through composites with other materials. For example, glass fibers, carbon fibers and other high-strength polymers have been used to reinforce PTFE's mechanical properties, though these reinforcement methods often lead to an increase in the material's coefficient of friction and a reduction in its chemical stability [6]. In contrast, PFA demonstrates better processability and mechanical properties. The partial incorporation of perfluoroalkyl side chains in PFA's structure enhances its mechanical strength and wear resistance compared to PTFE. Research indicates that PFA has higher tensile strength and impact resistance than PTFE [7-8]. Additionally, due to its excellent processability, PFA has gradually replaced PTFE in applications requiring high mechanical strength. However, PFA exhibits a slightly higher coefficient of friction and weaker hydrophobicity compared to PTFE [9].

To integrate the advantages of PTFE and PFA, increasing attention has been given in recent years to the preparation and performance of PTFE/PFA composite coatings. Studies have shown that by optimizing the PTFE/PFA ratio and incorporating composite materials, the mechanical properties and wear resistance of coatings can be significantly improved. In 2011, DuPont introduced a new high-temperature melt-processable resin, ECCtreme® ECA. This resin is composed of a dry blend of PFA and low molecular weight PTFE powder. Compared to fully or partially fluorinated fluoropolymers, ECCtreme® ECA demonstrates several exceptional properties: outstanding high-temperature and chemical resistance, excellent abrasion resistance, and no degradation of tensile modulus even after nearly two years of continuous exposure to 315 ℃. Additionally, it exhibits a dielectric constant similar to other melt-processable perfluoropolymers and a dissipation factor lower than standard PFA [10]. Ye Sujuan et al. prepared PTFE and PFA composites using carbon fiber (CF) and glass fiber (GF) as fillers. They investigated the effects of these fillers on the tribological and sealing performance of the composites. The results demonstrated that the addition of CF and GF enhanced the wear resistance of the composites, with wear rates reaching approximately 10^{-6} $mm^3/N\cdot m$. Furthermore, the sealing performance of PTFE/PFA composites was significantly improved. Notably, the wear rate of PFA/CF composites was much lower than that of PTFE composites, due to the unique structure of the transfer film at the coupled interface, which was thicker, smoother, and denser [11]. Gao Shuohong et al. investigated the effects of different ratios of PFA to Al_2O_3-40%TiO_2 (AT40) on coating properties. They found that the composite coatings exhibited granular protrusions with circular and elliptical shapes on the surface. These protrusions featured micro/nano binary papillary structures resembling those on a lotus leaf, which endowed the coatings with excellent hydrophobicity.Additionally, increasing the ceramic phase content in the coating resulted in increased surface roughness, friction coefficient, microhardness and bond strength [9]. Therefore, coatings with a higher PTFE content exhibit superior hydrophobicity and lower friction coefficients, while coatings with a higher PFA content demonstrate better wear resistance and bond strength. Moreover, the microstructure of the coating surface plays a critical role in its tribological properties. Research indicates that composite coatings with higher PTFE content tend to have rougher surfaces, which enhance hydrophobicity but may increase the friction coefficient. In contrast, the addition of PFA results in smoother surfaces, reducing the friction coefficient but weakening hydrophobicity.

In the field of tribology, the coefficient of friction and wear resistance are critical indicators for evaluating material performance. PTFE/PFA composite coatings have garnered increasing attention due to their excellent antifriction and wear-resistant properties [11]. For instance, under high-load conditions, composite coatings with a higher PFA content exhibit superior wear resistance and lower wear rates. Conversely, for low-load applications requiring a low coefficient of friction, coatings with a higher PTFE content are more suitable. Some studies have also explored the performance of composite coatings in specialized environments. This makes such coatings highly promising for applications in fields such as marine engineering, construction and aerospace [12]. Although significant progress has been made in the study of PTFE/PFA composite coatings, many issues remain to be addressed. For example, the mechanism by which the microstructure of composite coatings affects their tribological properties requires further investigation to better design coatings with specific functionalities. Changes in the surface microstructure of the coatings can significantly influence their wettability and tribological performance. Therefore, this study aims to prepare PTFE/PFA composite coatings with varying ratios and to investigate the relationships among the coatings' microstructure, wettability and tribological properties.

2. Experimental Methods

2.1 Preparation Method of PTFE and PFA Composite Coatings

In this study, PTFE and PFA composite coatings with different mass ratios were prepared using the solution blending method. The method is designed to ensure that the composite coatings exhibit good uniformity and structural stability. The preparation steps are as follows: First, according to the experimental design, different amounts of PTFE and PFA powders are weighed; then the powders are separately added to a polyimide (PI) resin solvent. This resin solvent is composed of 20% polyimide dissolved in 80% N-Methyl-2-pyrrolidone (NMP) solvent. To ensure the uniformity of the mixture, a high-speed stirrer is used to mix the solution at 2000 rpm for 10 minutes, until a uniform dispersion is formed in the solution. The detailed experimental parameters are shown in Table 1.

Table 1 Preparation Parameters of PTFE/PFA Composite Coatings.

No.	Mass ratio (PI/PTFE/PFA)	Coating thickness (μm)	Heat treatment temperature (℃)	Heat treatment time (min)
1	50:50:0	50	350	60
2	50:33.33:16.67	50	350	60
3	50:25:25	50	350	60
4	50:16.67:33.33	50	350	60
5	50:0:50	50	350	60

After obtaining a homogeneous coating mixture, a compressed air spray gun was used to evenly spray the coating onto aluminum substrates with a thickness of 4 mm. During the spraying process, the spraying time was adjusted to precisely control the dry film thickness of the coating, ensuring that the final film thickness was approximately 50 microns. It was important to ensure that the coating covered the substrate surface evenly, avoiding uneven thickness or coating defects. After spraying, the samples were placed in a high-temperature forced air-drying oven. The samples were initially baked at 80 ℃ for 1 hour to remove the solvent from the coating. Then, the temperature was slowly increased to 350 ℃ within 90 minutes and maintained at this temperature for 60 minutes to ensure complete curing of the coating. The appropriate heating rate and holding time were controlled to ensure the structural stability and mechanical properties of the composite coating. After the heat treatment, the samples were naturally cooled to room temperature to obtain uniform and dense coating samples. By strictly controlling the component ratios, coating thickness, heat treatment temperature and time, PTFE/PFA composite coatings with different properties were prepared. For ease of subsequent analysis and discussion, the composite coatings with different ratios were numbered from 1# to 5# as shown in Table 1, with the PFA content increasing as the numbers increase.

2.2 Wettability Test Method

In this experiment, a CA80 contact angle goniometer (Figure 1) was used to perform water contact angle measurements on PTFE/PFA composite coatings with different ratios to assess their hydrophobic properties. During the test, a drop of deionized water was placed on the surface of the coating, and the contact angle at the point where the water droplet contacts the coating surface was measured. Generally, a larger contact angle indicates better hydrophobic performance of the coating. By measuring the contact angles of coatings with different ratios, the variation in surface hydrophobicity with changing material ratios can be quantitatively analyzed.

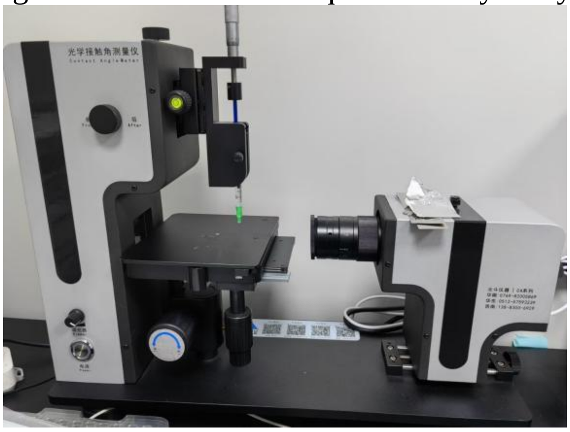

Figure 1 The CA80 contact angle goniometer.

2.3 Tribological Test

The friction coefficient and wear rate of the composite coating were evaluated under dry friction conditions using an MRH-3 high-speed ring-on-block friction and wear testing machine as shown in Figure 2. The counterface material was a 304 stainless steel ring with an outer diameter of 50 mm. The friction test parameters were as follows: an applied load of 20 N, a rotational speed of 95 rpm (corresponding to 0.5 m/s linear speed), and a test duration of 30 minutes. The friction coefficient was recorded in real time during the test using a pressure sensor, while the specific wear rate was calculated based on measurements of the wear scar width.

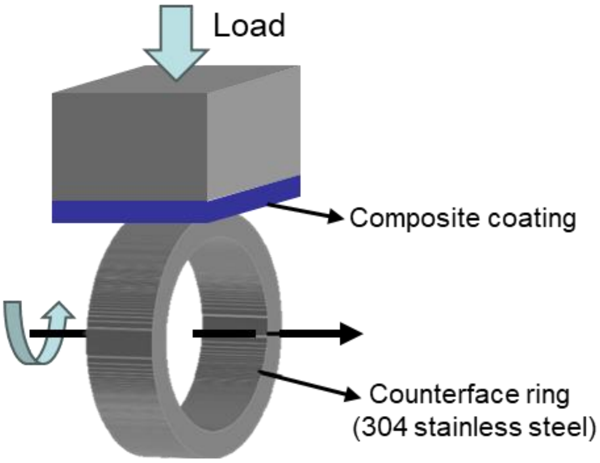

Figure 2 Schematic diagram of the testing principle for the ring-on-block tribometer.

2.4 Surface Morphology and Roughness Analysis

To comprehensively characterize the surface morphology and roughness of polytetrafluoroethylene (PTFE) and perfluoroalkyl ethylene (PFA) composite coatings, a Profilm3D benchtop optical profiler was employed for microscopic observation and the analysis of the coating surfaces. This instrument enables non-destructive three-dimensional surface profiling and provides high-resolution images of the surface structure, allowing for precise roughness evaluation. Multiple regions on each sample were selected for measurement to ensure the representativeness of the data. The surface irregularity was quantified using the average roughness value (Ra). By analyzing the roughness values of coatings with different compositions, insights into the relationship between surface properties and tribological performance were obtained.

2.5 Adhesion Strength Testing of the Coating

To evaluate the adhesion strength between the composite coating and the substrate, a scratch tester was employed. The scratch test is a widely used standard method for assessing coating adhesion by gradually increasing the loading force of the indenter to simulate the peeling or damage process of the coating under actual application conditions. During the experiment, a diamond-tipped stylus applied a linearly increasing load to the coating surface. The load-displacement curve was recorded throughout the scratch process, and the critical load (Lc), at which the coating began to crack or delaminate, was determined using acoustic emission signals and microscopic observation. This critical load quantitatively reflects the adhesion strength between the coating and the substrate.

3. Results and Discussion

3.1 Wettability

Wettability refers to the ability of a material’s surface to adsorb and spread liquids, which is generally related to its surface energy. Lower surface energy corresponds to poorer wettability, making it more difficult for liquids to spread on the surface. PTFE possesses an extremely low surface energy of approximately 18.5 mN/m, which imparts its strong hydrophobicity and non-stick properties. Liquids form distinct bead-like droplets on its surface, resisting spreading. PFA, with a slightly higher surface energy of 18.0–20.0 mN/m, also exhibits low wettability, forming relatively large contact angles on its surface, although these angles are slightly lower than those on PTFE [13].

As illustrated in Figure 3, the composite coatings with various formulations exhibited excellent hydrophobic properties. Notably, Samples 2–4 demonstrated outstanding performance, with contact angles exceeding 135°. The contact angle measurements revealed a trend of initial increase followed by a decrease with the increasing PFA content. This behavior is likely closely related to the differences in hydrophilicity and hydrophobicity between the components and the microstructure of the coating surface. Specifically, variations in the chemical properties and proportions of the components significantly influence the surface energy of the coating, thereby altering its wettability. Interestingly, the results of this study indicate that with higher PFA content, it has a higher surface energy. The contact angle of the composite coating does not monotonically decrease but instead exhibits an initial rise followed by a decline.

This phenomenon can be attributed to a secondary factor influencing contact angles—surface microstructure. For instance, coatings with higher surface roughness may lead to larger contact angles due to micro- or nanoscale surface structures that form air pockets, enhancing hydrophobicity. This effect causes liquids to form irregular interfaces under the influence of the microstructure, reducing the wetting area and further enhancing hydrophobicity. Thus, the variations in contact angle reflect not only changes in surface energy but also the complex interplay between the coating's microstructure and wettability.

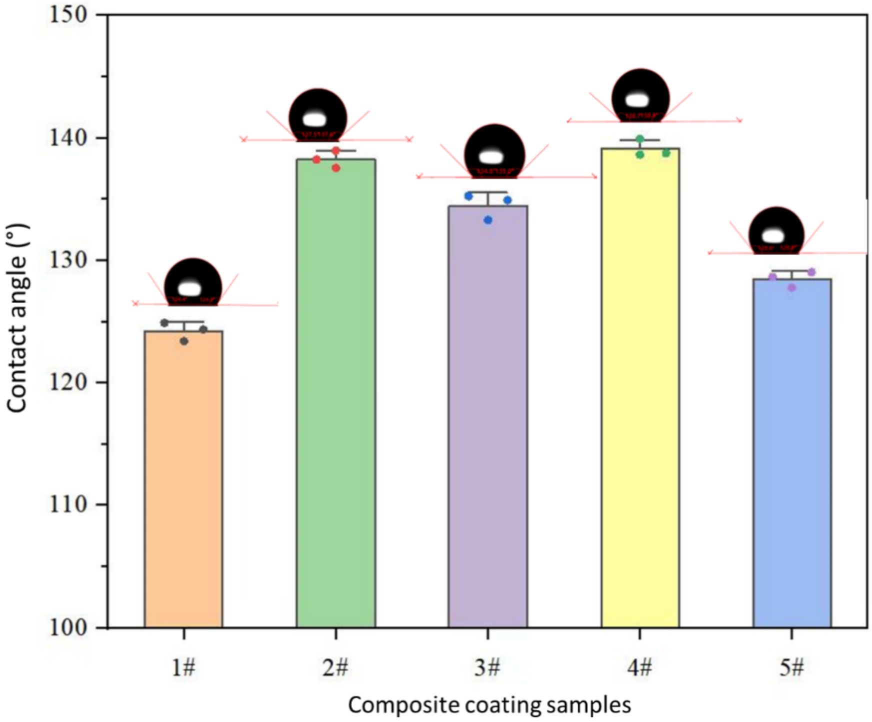

Figure 3 Contact angle test results of composite coatings with different formulations.

3.2 Morphology and Roughness of Composite Coatings

To further understand the wettability and contact angle variation mechanisms of composite coatings with different PTFE/PFA ratios, a 3D profilometer was performed to examine their surface morphology and calculate roughness values. The results are shown in Figures 4 and 5, respectively. The 3D surface morphology images of composite coatings with varying PTFE/PFA ratios reveal significant differences in surface structure at the microscale. Surface roughness exhibits a noticeable trend with increasing PFA content. Specifically, Sample 1 displays a relatively smooth surface with low roughness and minimal height differences between surface protrusions and depressions. This smooth structure corresponds to lower roughness values, indicating that the coating surface remains relatively uniform without the addition of PFA. Consequently, the low roughness of Sample 1 results in a contact angle consistent with PTFE's inherent hydrophobic range. However, the high flatness limits the potential for further increases in the contact angle.

With the addition of PFA (e.g., Samples 2–5), the coating surface progressively develops more pronounced microscopic protrusions and depressions, leading to a significant increase in roughness. For instance, Sample 3 exhibits distinct microscopic rough structures. This increased roughness correlates with larger contact angles, suggesting that changes in surface morphology effectively enhance the hydrophobic performance of the coating. This phenomenon can be explained using the Wenzel model, which posits that rough surfaces amplify a material's inherent hydrophobic characteristics. Although higher PFA content may decrease the material's intrinsic hydrophobicity, the increased surface roughness exerts a greater influence on wettability within a certain range. Notably, in Sample 5, despite the roughness not decreasing significantly, the complete substitution of PTFE with PFA results in a marked reduction in contact angle. This indicates that while PFA exhibits some hydrophobicity, its roughness is insufficient to increase the contact angle substantially.

Thus, further increases in PFA content may weaken hydrophobic performance, which is consistent with the contact angle results for Sample 5.

In summary, the contact angle trends of composite coatings depend not only on surface energy but also on surface roughness. Changes in surface morphology, controlled through roughness, can effectively enhance or suppress the hydrophobicity of the coating. The correlation between coating roughness and contact angle demonstrates that a rational design of PTFE and PFA ratios can optimize the coating's microstructure, enabling precise control over its wettability. This result provides a theoretical foundation and experimental support for further improving the surface properties of composite coatings.

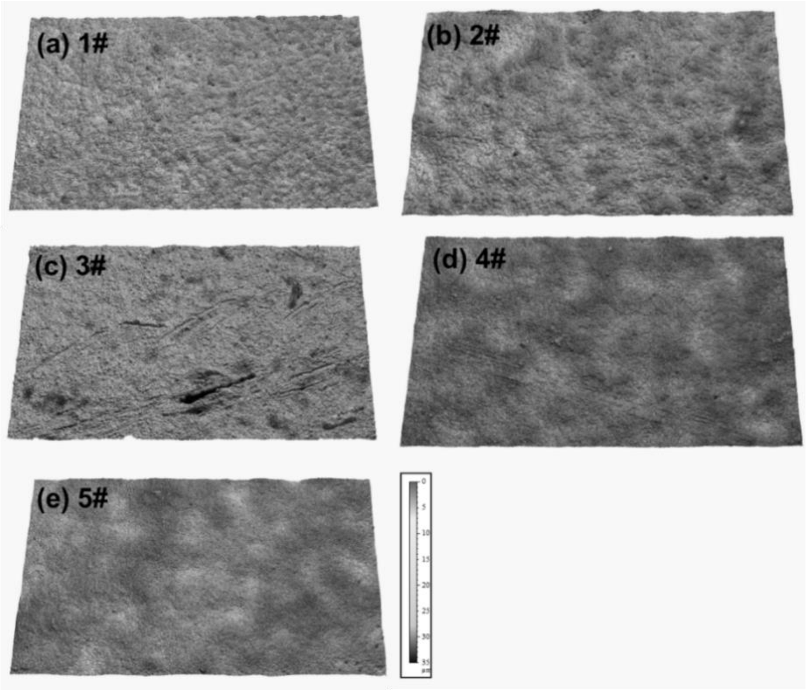

Figure 4 Surface morphology images of composite coatings with different ratios.

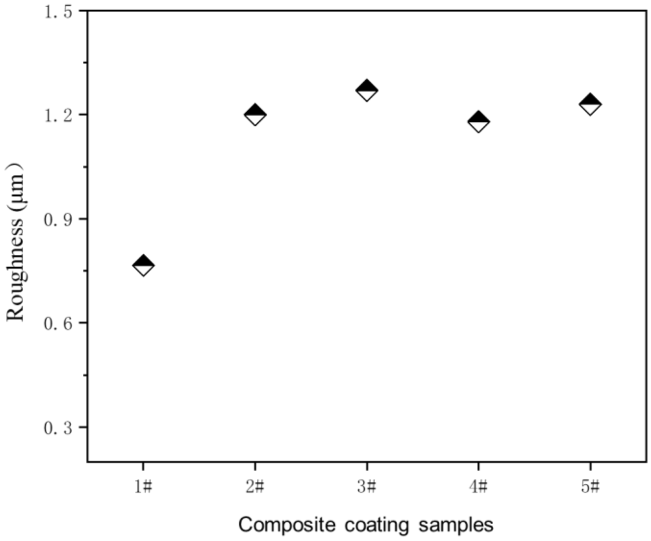

Figure 5 Surface roughness results of composite coatings with different ratios.

3.3 Adhesion Test Results

The adhesion test was conducted to evaluate the bonding strength between the PTFE/PFA composite coatings and the substrate. To quantify the adhesion strength, a scratch test method was employed, using a scratch tester to apply a progressively increasing load on the coating surface. This test simulated the peeling or damage process experienced by the coating during actual use. The scratch morphology was analyzed through microscopic observation of wear tracks to assess the cracking and delamination behavior of the coating under stress. As shown in Figure 6, all samples exhibited varying degrees of cracking along the scratch tracks. In Sample 1#, the white substrate was exposed at the early stage of scratching. However, with the increasing PFA content, the scratch morphology of the coatings gradually improved. Notably, in Sample 5#, the substrate remained unexposed even at the end of the scratch, indicating excellent adhesion strength.

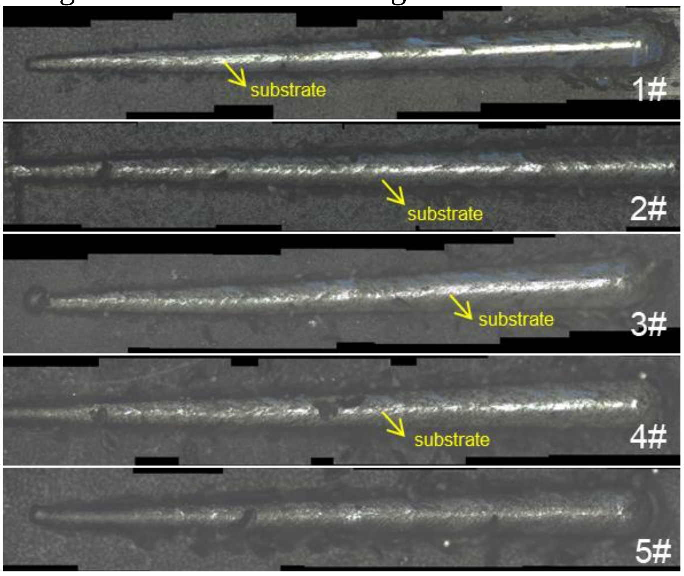

Figure 6 Surface scratch images of composite coatings with different ratios.

3.4 Tribological Performance

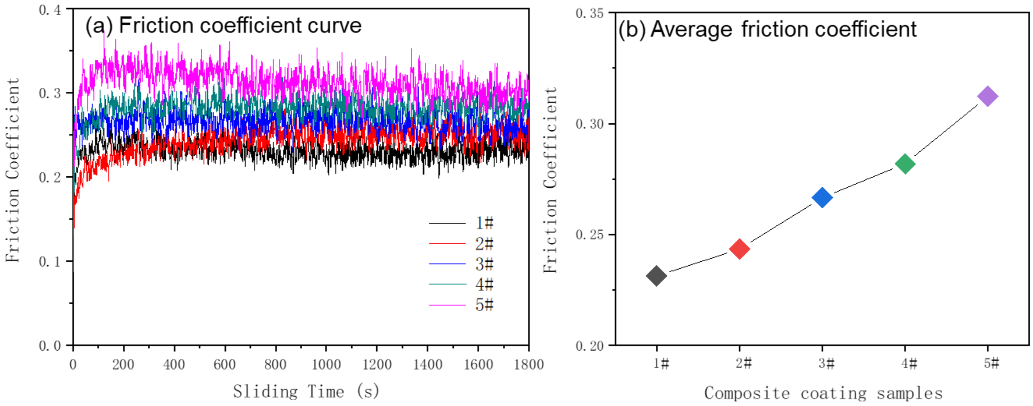

Figure 7 Friction coefficient curves of composite coatings with different ratios.

The coefficient of friction (COF) is a critical parameter for evaluating the sliding resistance of materials, reflecting their antifriction capability during the friction process. The COF curve of

PTFE/PFA composite coatings with different ratios was measured through friction and wear tests, as shown in Figure 7. The results indicate that coatings with a higher PTFE content (e.g., Samples 1 and 2) exhibited lower COF values during testing, ranging from approximately 0.20 to 0.25. This is attributed to the tightly packed fluorine atoms in the molecular structure of PTFE, which result in extremely low surface energy. The reduced surface energy minimizes adhesion between the material and the counterpart, conferring excellent self-lubricating properties [14]. As the proportion of PFA increased, the COF gradually rose, reaching about 0.32 for Sample 5. This trend can be explained by the stronger intermolecular forces of PFA compared to PTFE, leading to increased hardness and wear resistance. However, higher hardness and surface energy of PFA contribute to greater sliding resistance.

To better evaluate the wear resistance of the coatings, the wear rate was calculated by measuring the width and depth of wear tracks, as shown in Figure 8. The wear rate of Sample 1, without added PFA, was relatively high at approximately 4.19×10^{-6} mm^3/Nm. This is due to the lower hardness of PTFE, which makes it more prone to mechanical removal during friction, resulting in larger wear scars. With the addition of PFA, the hardness and adhesion strength of the composite coatings improved, significantly enhancing wear resistance. However, an excessive PFA content was found to reduce wear resistance. This suggests that the optimal balance between PTFE and PFA is crucial for achieving superior tribological performance [15].

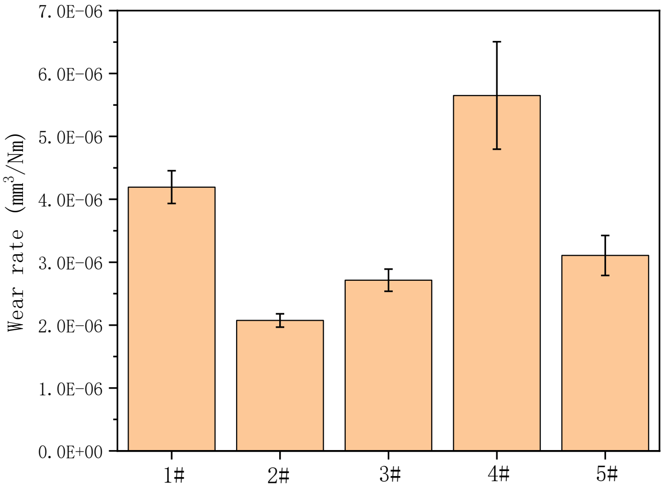

Figure 8 Wear rate of composite coatings with different ratios.

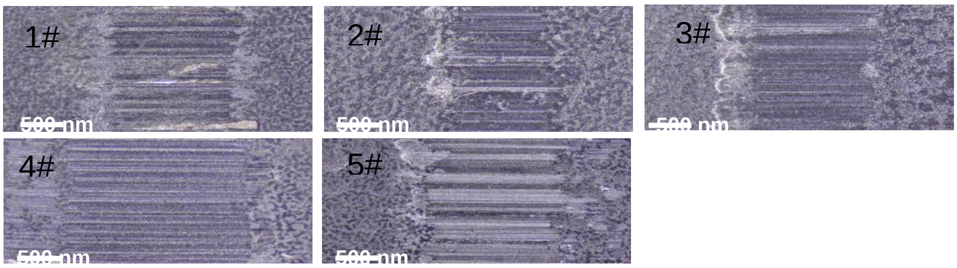

Figure 9 The wear track morphology of composite coatings with different ratios.

To further analyze the wear mechanism of the composite coatings, Figure 9 presents the surface wear morphology of the coatings. For Sample 1, dominated by PTFE, the wear tracks are relatively smooth. Although the wear tracks are wider, the wear is uniform. With the increasing PFA content, the wear tracks exhibit characteristic grooves, primarily due to the higher hardness of PFA. During the friction process, the wear debris acts as abrasive particles, contributing to micro-abrasion. Notably, for Sample 5, which contains the highest proportion of PFA, the wear track width is narrower, but the groove features within the wear tracks are more pronounced.

These results indicate that the addition of PFA not only improves the hydrophobicity of the coatings but also significantly enhances their adhesion strength and wear resistance. However, excessive PFA content increases the roughness and friction coefficient of the composite coating, which negatively impacts its tribological performance. Therefore, in practical applications, the ratio of PTFE to PFA must be carefully controlled to achieve a balanced combination of low friction and wear resistance properties. In this study, the composite coating (Sample 2) demonstrated the best overall performance, achieving a contact angle of 138°, a friction coefficient of approximately 0.23, and a wear rate as low as 2.07×10^{-6} mm^3/Nm. This is similar to the wear rate results obtained by Ye Sujuan et al. who prepared PTFE and PFA composites using carbon fiber (CF) and glass fiber (GF) as fillers. [12]

4. Conclusion and Outlook

This study systematically investigated the wettability and tribological properties of composite coatings by adjusting the ratio of PTFE to PFA. The results show that the surface roughness of the coating is a key factor in influencing its coefficient of friction and wettability. The addition of PFA increases the surface roughness and significantly enhances hydrophobicity. However, excessive PFA content may, to some extent, hinder further improvements in hydrophobicity. Moreover, the incorporation of PFA strengthens the adhesion between the coating and substrate. Although it slightly increases the friction coefficient of the composite coating, it significantly improves wear resistance, making the coating more suitable for practical applications.

Therefore, future research could focus on further optimizing the microstructure of the coatings and exploring the impact of different component ratios on tribological and wettability properties to achieve more desirable coating performance. Additionally, durability and environmental adaptability tests based on potential operational conditions of the composite coatings should be a key focus in future research. Such studies will provide a stronger theoretical foundation for the performance of composite coatings in practical applications and contribute to the continuous development of this field.

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