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Article

The Effect of Coating Additives on the Properties of Hydrophobic Coatings with Low Infrared Emissivity

Weigang Zhang *, Xiang Li and Dandan Lv

College of Materials and Chemical Engineering, Chuzhou University, Hui feng Road 1, Chuzhou 239000, China
* Correspondence: abczwg15@chzu.edu.cn

Abstract: In order to further reduce the emissivity of hydrophobic low infrared emissivity composite coating and improve its mechanical properties, a dispersant, adhesion enhancer, and defoamer were used to improve the dispersion state of the fillers, the interface structure, and the surface state of a hydrogen silicone oil-modified polyurethane/Al composite coating. The influences of dispersant, adhesion enhancer, and defoamer on the microstructure, emissivity, glossiness, hydrophobic property, adhesion strength, and impact strength of the coating were systematically studied. The results indicate that polycarboxylate anionic dispersant can improve the dispersion state of Al powder and nano-SiO$_2$ in the coating, so that the infrared emissivity of the coating can be reduced, and the coating can have greater hydrophobic and mechanical properties. The bonding strength between the resin and the substrate of the coating can be improved by the adhesion enhancer through a bridging action, so that the mechanical properties of the coating can be significantly improved. The defoamer can significantly reduce the pores in the coating, resulting in a substantial improvement in the surface condition, and the mechanical properties can be significantly improved. The coating exhibits superior characteristics, including an emissivity value of 0.527, glossiness of 4.3, adhesion strength of grade 1, impact strength of 40 kg cm, and hydrophobic property (the water contact angle (WCA) is 140°) when the amount of dispersant, adhesion enhancer, and defoamer is 5 wt%, 4 wt%, and 1 wt%, respectively.

Keywords: composite coating; infrared emissivity; hydrophobic property; mechanical property

1. Introduction

In recent years, in order to meet the needs of high-speed penetration in modern war, various types of aircraft have greater and greater engine power and faster and faster flight speed, which make the infrared radiation characteristics of various types of aircraft caused by thermal and aerodynamic heating in the process of high-speed flight more and more obvious. The high infrared radiation characteristics of various types of aircraft are easy to be found by enemy detection equipment, such as an infrared thermal imager, and destroyed by infrared-guided weapons in wartime [1]. In view of this, numerous scholars have shown great interest in low infrared emissivity materials that can effectively diminish infrared radiation characteristics across various aircraft types [2–7]. Among all the kinds of low-emissivity materials reported, resin/metal composite coatings, which are composed of various resin matrix and flake metal pigments, have obvious comparative advantages in terms of low emissivity, engineering application performance, multi-spectrum compatibility, cost, and convenience [8–12] and have been developed rapidly. In the field of infrared stealth equipment, such as land, sea, and air, it has a considerable application prospect. However, the resin/flake metal composite coating reported at present mainly uses polyurethane (PU), epoxy resin, and other strong polar resins as the main film-forming materials [13–15]. The main advantage of the coating prepared by the above resin matrix is that it has good mechanical properties. However, the strong hydrophilic polar groups, such as the isocyanate group, carbonyl group, and epoxy group, present in large quantities in the molecular structure of the resin matrix easily make the prepared low emissivity coating...
have a high surface energy, so it cannot show good hydrophobic properties. Thus, the coating encountered a new bottleneck problem in terms of anti-pollution concerns [16]. It is an effective method to solve the above problems to make the above coating have good hydrophobic properties through certain technical means [17,18].

Coatings with prominent hydrophobic properties have broad application prospects in many fields [19,20]. In the process of coating preparation, the super-hydrophobic properties are mainly realized by reducing the surface energy of the coating and constructing micro- and nano rough structures [21,22]. In an early stage, our research group used polydimethylsiloxane (PDMS) as a low surface energy resin matrix, flake Al powder as functional pigment, and nano-SiO₂ to construct the micro–nano rough structure; a low emissivity coating with outstanding hydrophobic properties was preliminarily prepared [23]. However, the emissivity of the coating reaches 0.661, while the mechanical properties are poor; especially the adhesion strength and impact strength are very low, so there is still a large area for improvement in terms of the engineering application requirements. In view of this, it is of great significance to further reduce the emissivity and improve the mechanical properties of the hydrophobic coating by certain technical means. In this paper, polyurethane modified by hydrogen-containing silicone oil (HCSO) is used as the resin matrix, and coating additives such as dispersant, adhesion enhancer, and defoamer are used to modify the coating interface, so as to optimize the low emissivity, adhesion strength, and impact strength of the coating on the premise of ensuring that the coating has good hydrophobic properties. In this paper, it is expected that the coating has more prominent low emissivity, adhesion strength, and impact strength under the premise of maintaining good hydrophobicity through the optimization of the coating formulation and comprehensive modification of various additives.

2. Materials and Methods

2.1. Materials

Nano-SiO₂ (purity 99.5 wt%, particle size 30 ± 5 nm); Al powders (solid content 67 wt%, flake, particle size 20–30 µm); PU (solid content 50 wt%); hydrogen-containing silicone oil (HCSO, liquid, solid content 96 wt%); medium molecular weight sodium polycarboxylate anionic surfactant, which was used as a dispersant (analytically pure); 2-hydroxyethyl methacrylate phosphate, which was used as an adhesion enhancer (analytically pure); dimethylsilicone oil, which was used as a defoamer (analytically pure); and tinplate substrate (12 cm × 5 cm × 0.3 mm) were purchased from NSPL Company, China. All other reagents used are analytically pure.

2.2. Preparation of the Coating

The tinplate plate (12 cm × 5 cm × 0.3 mm) was taken as the coated substrate and sanded so that its surface has obvious rough marks; then the surface of the substrate was wiped with a disposable paper towel dipped in an appropriate amount of anhydrous ethanol. The modified resin was obtained by combining HCSO and PU with a mass ratio of 2:8, and the resin matrix was used as an adhesive to prepare a hydrophobic low emissivity coating. The mass ratio of Al powder to nano-SiO₂ was set at 6:4, and a proper amount of modified resin and functional fillers (Al powder + nano-SiO₂) were measured in a disposable plastic cup, also in a 6:4 mass ratio. After adding an appropriate amount of anhydrous ethanol, the paint was stirred and dispersed evenly with a glass rod until no significant granular material was visible in the paint. Then the paint was treated with ultrasonic shock at a frequency of 25 KHz for 10 min, so that the paint is uniform and fine. The paint was coated on the tinplate by glass rod scraping, air dried for 3 h, and cured at 80 °C for 3 h to obtain the coating sample, and then the properties were characterized. On the basis of the above basic formula samples, the dispersant was added by 1%, 3%, 5%, and 7% (mass fraction) of the total filler content, and the effect of the dispersant on the comprehensive properties of the coating was studied. On the basis of the above optimal amount of dispersant, the adhesion enhancer was added according to 2%, 3%, 4%, and
5% (mass fraction) of the total resin matrix, and the influence of adhesion enhancer on the comprehensive properties was studied. Then, on the basis of the optimal amount of adhesion enhancer, the defoamer was added according to 1%, 3%, and 5% (mass fraction) of the resin matrix, and the effect of the defoamer on the comprehensive properties was studied. The preparation process of the hydrophobic composite coating with low emissivity and good mechanical properties is shown in Figure 1.

![Figure 1. Schematic for the preparation of the coating.](image)

2.3. Characterization

The surface morphology of the coating was characterized via scanning electron microscopy (SEM, JSM-6510 LV). The infrared emissivity (8~14 µm) of the coating was measured using an IR-2 infrared emissometer; the test error is ±0.02. The glossiness of the coating was measured using the mirror glossiness tester (JGKZ-60); the test error is ±0.3. The water contact angle (WCA) of the coating was measured using a contact angle meter (JC2000D7); the test error is ±0.5°. A 3 µL water droplet was formed on the surface of the coating by a manual sampling method. The WCA of the water droplet was measured by the software of the instrument. The adhesion strength of the coating was evaluated by using the QFZII circle-cut tester (China) according to GB 1720-79(89). This method evaluates the adhesion strength of the coating by the degree of damage caused by the scratches on the coating. The adhesion strength is divided into 7 levels, from grade 1 to grade 7; the adhesion strength gradually decreases. The impact strength of the coating was evaluated by using the QCJ impact strength tester (China) according to GB 1732-93. In this approach, the impact strength of the coating is evaluated by observing the condition of the coating after being struck at varying heights with a 1 kg hammer. The higher the height that can withstand the impact of the hammer, the higher the impact strength of the coating. The maximum index value of the impact strength is 50 kg-cm.

3. Results and Discussion

3.1. Effect of Dispersant on Coating Performance

Figure 2 demonstrates the SEM images of the coatings with varying amounts of dispersant. When a specific amount of dispersant is added to the coating, it becomes...
apparent that the dispersion of flake Al powder and nano-SiO₂ particles in the coating is significantly enhanced. The characteristics of flake Al powder on the coating surface are more obvious, and the agglomeration characteristics of nano-SiO₂ are reduced to a certain extent. In addition, the addition of dispersants to the coating does not have a negative effect on the regularity of the coating surface. The coating will exhibit relatively low emissivity due to the enhanced reflection of infrared light, resulting from the prominent flake-like Al powder characteristics on its surface [12]. The improved dispersion of nano-SiO₂ in the coating contributes to the development of a more pronounced micro–nano papilloid structure on the coating surface, enhancing the hydrophobicity of the coating [22].

The optical and mechanical properties of the coating generally decreases as the amount of dispersant added to the coating increases. In contrast, the glossiness generally showed an upward trend. When the addition amount of dispersant increases to 3 wt%, the infrared emissivity of the coating can be reduced to 0.535, which is 8.55% lower than the original emissivity (0.585). The corresponding glossiness of the coating can be increased from 3.0 to 4.8. However, the coating has polar glossiness characteristics under varying amounts of dispersant. The aforementioned performance indexes can enable the coating to possess excellent infrared and visible stealth capabilities. The change of properties is mainly caused by the microstructure of the coatings under varying amounts of dispersant. By modifying the coating with dispersant, the dispersion state of flake Al powder in the coating can be more uniform. Consequently, the surface characteristics of the coating’s flake Al powder become more pronounced, thereby enhancing the coating’s ability to reflect infrared light and reducing its infrared emissivity [12]. The increase in glossiness of the coating is also caused by the obvious characteristics of flake Al powder in the coating. On the other hand, the coating consists of numerous micro–nano rough structures made up of nano-SiO₂ particles, resulting in a high overall roughness that helps maintain the coating’s extremely low glossiness [22]. Good mechanical properties are a basic requirement for the application of a stealth coating. Hence, we conducted tests on the adhesive strength and impact resistance of the coating using various quantities of dispersant, and the outcomes are presented in Table 1. With the increase in the amount of dispersant added to the coating, the adhesion strength and impact strength of the coating have been significantly improved.
When the amount of dispersant in the coating increases to 5 wt%, the adhesion strength and impact strength of the coating can be improved from grade 5 and 10 kg·cm to grade 2 and 20 kg·cm, respectively.

Table 1. Performance indexes of coatings with varying amounts of dispersant.

<table>
<thead>
<tr>
<th>Amounts of Dispersant/wt%</th>
<th>Emissivity</th>
<th>Glossiness</th>
<th>Adhesion Strength/Grade</th>
<th>Impact Strength/kg·cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.585</td>
<td>3.0</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>0.583</td>
<td>4.3</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>0.535</td>
<td>4.8</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>0.538</td>
<td>5.0</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>0.541</td>
<td>5.4</td>
<td>2</td>
<td>20</td>
</tr>
</tbody>
</table>

The WCA of the coating, the optimal amount of dispersant is determined to be 5 wt%. When the amount of dispersant in the coating increases to 5 wt%, the adhesion strength and impact strength of the coating have been improved. The WCA increased from 132° before modification to 139° after modification, and with continued increase in the amount of dispersant, the WCA decreases slightly with the increase in the addition amount of dispersant. The above results show that adding a small amount of dispersant to the coating can obviously improve the hydrophobic property of the coating. Considering the infrared emissivity, glossiness, adhesion strength, impact strength, and WCA of the coating, the optimal amount of dispersant is determined to be 5 wt%.

Figure 3. WCA of the coatings with varying amounts of dispersant: (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%, (e) 7 wt%.

3.2. Effect of Adhesion Enhancer on Coating Performance

In order to further improve the emissivity, adhesion strength, and impact strength of the coating, the effects of adhesion enhancer on the properties were studied based on the addition amount of dispersant fixed at 5 wt%. Figure 4 displays the SEM images of the coatings that possess varying quantities of adhesion enhancer. The addition of an adhesion enhancer appears to have minimal impact on the coating’s microstructure. Before and after the modification of the adhesion enhancer, the distribution of Al powder and nano-SiO$_2$ in the coating almost did not change, and the coating still maintained a relatively regular surface state. These microstructure states are conducive to the coating maintaining relatively stable optical and hydrophobic properties.

Table 2 demonstrates the optical and mechanical characteristics of the coating with varying quantities of adhesion enhancer. The infrared emissivity of the coating decreases slightly with the increase in the addition amount of adhesion enhancer. The infrared emissivity decreased slightly from 0.538 before modification to 0.508 after modification when the content of adhesion enhancer increased to 3 wt%. However, the glossiness has no obvious change rule with the change in the amount of adhesion enhancer added in the coating. The glossiness of the coating can be adjusted in a small range of 5.0 to 6.1; it still maintains a very low gloss characteristic. The main reason is that the adhesion enhancer used in this paper has special bridging characteristics. One end of its molecular structure contains strong polar groups such as hydroxyl, which can be fused with functional...
fillers with high surface energy in the coating. The other end of its molecular structure contains weakly polar groups such as phosphate groups, which can be fused with the resin matrix with low surface energy in the coating. The addition of the adhesion enhancer significantly improves the bond between the resin matrix and the functional pigment in the coating, leading to improved coating uniformity and reduced coating emissivity [12]. However, the adhesion enhancer only has a minimal impact on the coating’s surface condition, consequently resulting in little to no change in the coating’s glossiness. On the other hand, the adhesion enhancer also has an obvious promoting effect on the adhesion strength and impact strength of the coating. After modification, the addition of a 4 wt% adhesion enhancer in the coating improves the adhesion strength from grade 2 to grade 1 and the impact strength from 20 kg cm to 30 kg cm. The effect of adhesion enhancer on the mechanical properties of the coating is consistent with that reported in the related literature [24]. The main reason is that the adhesion enhancer can significantly enhance the bonding strength between the resin matrix and the substrate, as well as the bonding strength between the resin matrix and functional fillers, through its bridging action. As a result, the mechanical properties can be substantially enhanced.

![SEM images of coatings with varying amounts of adhesion enhancer: (a,c) 0 wt%, (b,d) 4 wt%](image)

**Figure 4.** SEM images of coatings with varying amounts of adhesion enhancer: (a,c) 0 wt%, (b,d) 4 wt%.

**Table 2.** Performance indexes of coatings with varying amounts of adhesion enhancer.

<table>
<thead>
<tr>
<th>Amounts of Adhesion Enhancer/wt%</th>
<th>Emissivity</th>
<th>Glossiness</th>
<th>Adhesion Strength/Grade</th>
<th>Impact Strength/kg cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.538</td>
<td>5.0</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>0.520</td>
<td>5.6</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>0.508</td>
<td>5.7</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>0.508</td>
<td>5.0</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>0.511</td>
<td>6.1</td>
<td>1</td>
<td>30</td>
</tr>
</tbody>
</table>

Figure 5 shows the WCAs of the coatings with varying amounts of adhesion enhancer. The WCA of the coating decreases with the increase in the adhesion enhancer in the coating. The reason is that the molecular structure of the adhesion enhancer has strong polar groups such as the hydroxyl group, which can increase the surface energy of the
coating surface, thus reducing the hydrophobicity. Considering the infrared emissivity, glossiness, WCA, and mechanical properties of the coating, the optimal addition amount of adhesion enhancer in the coating is 4 wt%.

![Figure 5](image_url)

**Figure 5.** WCA of coatings with varying amounts of adhesion enhancer: (a) 0 wt%, (b) 2 wt%, (c) 3 wt%, (d) 4 wt%, (e) 5 wt%.

### 3.3. Effect of Defoamer on Coating Performance

In order to further improve the impact strength of the coating, the effect of defoamer on the properties was systematically studied. The SEM images of the coating with varying amounts of defoamer are indicated in Figure 6. The addition of defoamer in the paint has a very obvious effect on the surface structure of the coating. Adding a small quantity of defoamer to the coating noticeably reduces its original pores, enhancing the regularity and surface quality of the coating. Moreover, the addition of defoamer did not change the horizontal orientation state of the flake Al powder and the dispersion state of nano-SiO$_2$. The above microstructure characteristics are conducive to further improving the impact strength of the coating on the premise of maintaining low emissivity and good hydrophobicity.

![Figure 6](image_url)

**Figure 6.** SEM images of coatings with varying amounts of defoamer: (a,c) 0 wt%, (b,d) 1 wt%.

The optical and mechanical properties of the coating with varying amounts of defoamer are indicated in Table 3. The addition of defoamer in the coating clearly affects the emissivity of the coating. The amount of defoamer increased in the paint leads to a gradual increase in the coating’s emissivity. It can be increased from 0.508 to 0.582, as the defoamer...
content is increased from 0 wt% to 0.582. The reason is that the molecular structure of the defoamer of dimethylsilicone oil has a large number of silico-oxygen bonds, which can produce strong absorption in the middle infrared band. Therefore, adding defoamer to the paint can enhance the absorption of infrared light and increase the emissivity of the coating [12]. The glossiness can be less than 5.0 under the conditions of different amounts of defoamer, which reflects the outstanding low gloss characteristics of the coating. Due to the modification of the paint by the defoamer, the porosity in the coating is obviously reduced, and the regularity is obviously increased, so the mechanical properties of the coating can be significantly improved. The addition of 1 wt% defoamer to the coating can increase the impact strength from 30 kg·cm to 40 kg·cm after modification (Table 3). The effect of defoamer on improving the mechanical properties of the coating is consistent with that reported in the related literature [25].

Table 3. Performance indexes of coatings with varying amounts of defoamer.

<table>
<thead>
<tr>
<th>Amounts of Defoamer/wt%</th>
<th>Emissivity</th>
<th>Glossiness</th>
<th>Adhesion Strength/Grade</th>
<th>Impact Strength/kg·cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.508</td>
<td>5.0</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>1</td>
<td>0.527</td>
<td>4.3</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>0.563</td>
<td>4.7</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>0.582</td>
<td>4.8</td>
<td>1</td>
<td>40</td>
</tr>
</tbody>
</table>

Figure 7 shows the WCAs of the coatings with varying amounts of defoamer. The WCA of the coating can be significantly increased after the coating is modified with defoamer; the hydrophobicity of the coating can be obviously improved. When the amount of defoamer added in the paint is 1 wt%, the WCA of the coating can be increased from 133° to 140°. The main reason is that the defoamer used in this paper is dimethylsilicone oil, which has the characteristics of low surface tension and low surface energy. Therefore, by adding a small amount of defoamer to the paint, the hydrophobicity of the coating can be increased [21].

Figure 7. WCAs of coatings with varying amounts of defoamer: (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%.

4. Conclusions

On the basis of HCSO-modified PU/Al composite coating, the dispersion state of various fillers in the coating is improved by a dispersant; the interfacial bond strength of the coating is improved by an adhesion enhancer; and the porosity of the coating is reduced by a defoamer. Finally, a low emissivity functional coating with good mechanical properties and hydrophobic properties is prepared. Polycarboxylate anionic dispersant can significantly enhance the dispersion of filler particles in the paint, thus reducing the emissivity and improving the hydrophobic property of the coating. The interface structure between the resin and fillers, and the interface structure between the resin and substrate, can be obviously improved by the adhesion enhancer. Thus, the bonding strength between the
resin and fillers, and the bonding strength between the resin matrix and tinplate substrate, can be enhanced. Then, the mechanical properties of the coating can be significantly improved. Adding a small amount of defoamer to the paint can obviously reduce the pores in the coating, so that the impact strength of the coating can be significantly improved. The impact strength of the coatings reported in this paper has not reached the highest possible, and the hydrophobic performance still has a large margin for improvement, which are two important issues worthy of further study.

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