Fangfang Wang, Lajun Feng*, Huini Ma, Zhe Zhai and Zheng Liu

Influence of nano-SiO₂ on the bonding strength and wear resistance properties of polyurethane coating

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Abstract: To improve the wear resistance of polyurethane (PU) coating and its adhesion to the steel substrate, a series of simple and practicable techniques were designed to mix nano-SiO₂ with PU powder to cast a coating layer onto the steel. When the addition of nano-SiO₂ was small, a network structure of PU-SiO₂ was produced. It improved the wear resistance of the composite coating and its adhesion to the steel substrate. When the addition of nano-SiO₂ was excessive, agglomerated nano-SiO₂ particles not only affected the bond between the PU resin and the steel substrate but also became abrasive materials, intensifying the abrasion of the composite coating during friction. It resulted in lower bonding strength and poorer wear resistance of the composite coating. The wear rate and friction coefficient of 2 wt.% SiO₂/PU composite coating were 1.52×10^{-6} cm³/min N and 0.31, respectively. Its wear resistance was about 10 times as high as that of the pure PU coating. Furthermore, a simple and practicable installation was designed to test the bonding strength between the coating and the steel substrate. The bonding strength between 2 wt.% SiO₂/PU composite coating and the steel substrate was 7.33 MPa, which was 39% higher than that of the pure PU coating.

Keywords: bonding strength; electrostatic spraying; nano-SiO₂; polyurethane coating; wear rate.

1 Introduction

The powder polyurethane (PU) coating is widely applied in areas such as surface decoration and corrosion protection due to its advantages of low toxicity, good corrosion resistance, good weather resistance, and high brightness [1–3]. However, the surface of PU coating can easily be scratched due to its poor wear resistance and low adhesion to the substrate. Furthermore, PU coating can easily be peeled off with large pieces in the case of collisions. Therefore, it cannot meet the protection requirements of wear resistance coating nowadays. It was reported that inorganic nanoscale particles could be used to improve the mechanical and physical properties of the polymer matrix [4–9]. Therefore, the incorporation of nanoparticles into PU, by an appropriate technique, is a promising approach to improve the properties of PU such as hardness, wear resistance, and bonding strength to the substrate. However, despite several years of research in this field, there is still a need to combine the suitable process with good mechanical properties.

Based on the reaction that occurred between the -NCO groups of PU and the -OH groups on the surfaces of nano-SiO₂ particles and some polar groups (such as the -NHCOO or -CONH groups) during curing at 200°C, a space network structure of organic/inorganic composite coating was formed [10–12], leading to the structure of the PU coating from linear crosslinking to network crosslinking. The network structure made the composite coating more compact. Thus, the bonding strength between the PU composite coating and the steel substrate was improved and its wear resistance was also greatly strengthened. In this work, a small amount of nano-SiO₂ was added into PU by a series of simple and practicable techniques. To improve the dispersion of nano-SiO₂ particles on the surfaces of PU particles and increase the interaction between them, the mixture was first dealt with a method of ball milling. Electrostatic spraying was applied to prepare a series of PU coatings [13]. The micrograph of untreated and treated nano-SiO₂ and the microstructure and properties of composite coatings were investigated by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscope (SEM).

*Corresponding author: Lajun Feng, School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, Shaanxi, China; and Key Laboratory of Corrosion and Protection of Shaanxi Province, Xi'an 710048, Shaanxi, China, e-mail: fenglajun@xaut.edu.cn

Fangfang Wang, Huini Ma, Zhe Zhai and Zheng Liu: School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, Shaanxi, China

2 Materials and methods

2.1 Material and specimen preparation

2.1.1 Material preparation

PU powder with an average diameter of 30–50 μm was supplied by Anyang Oubao Powder Coating Co., Ltd. Nano-SiO₂ (N-100) powder was supplied by Jining Huakai Resin Co., Ltd. The average diameter, specific surface area, and silica content of nano-SiO₂ were 40–60 nm, $300 \pm 25 \text{ m}^2/\text{g}$, and 99.8 m/m%, respectively.

Two different contents of nano-SiO₂ were mixed with PU powder (2 and 5 wt.%, respectively). The mixed powders were milled by a GN-2 high-energy ball mill for 1 h with a ball-to-powder mass ratio of 5:1. After that, the mixture was prepared to be sprayed.

Q235 steel with a dimension of $50 \times 20 \times 2 \text{ mm}$ was used as the metal substrate and was roughened by sand blasting treatment. The pressure of air was kept at $0.8 \pm 0.1 \text{ MPa}$. The distance between the Q235 steel substrate and the spray gun was controlled at $130 \pm 20 \text{ mm}$. The time of sand blasting treatment was 35 s. After that, the metal substrate was heated at 200°C for 5 min in an oven to remove any moisture.

2.1.2 Specimen preparation

The prepared mixture was sprayed onto the Q235 steel substrate to form a composite layer by a NEW KCI-CU801 electrostatic spraying equipment. Under same conditions, the pure PU powder was sprayed onto the Q235 steel substrate as the control sample. The voltage of electrostatic spraying was set at $55 \pm 5 \text{ kV}$. The pressure of compressed air was kept at $0.6 \pm 0.1 \text{ MPa}$. The distance between the Q235 steel substrate and the spray gun was controlled at $130 \pm 20 \text{ mm}$. Finally, the samples were cured at 200°C for 5 min in a curing oven and then taken out followed by cooling down to the room temperature.

The preparation of samples used in the bonding strength test was consistent with that of the above, and the only difference was that the Q235 steel substrate with a dimension of $50 \times 20 \times 2 \text{ mm}$ was replaced with Q235 steel wire with a diameter of 2 mm. The average thickness and length of the coating were 0.2 and 2 mm, respectively.

2.2 Characterization

2.2.1 Morphology analysis

The morphologies of untreated nano-SiO₂ particles and PU particles and the dispersion of nano-SiO₂ on the surfaces of PU particles after mechanical ball milling were observed by a JSM-6700F SEM.

2.2.2 FTIR

First, small parts of coatings were derived from the samples and then homogeneously mixed with KBr at a mass ratio of 1:100, respectively. The mixture was pressed into a thin sheet. An Alpha FTIR spectrometer was used to characterize the chemical structure of the coatings at room temperature, and its scanning range was $4000\text{--}500 \text{ cm}^{-1}$.

2.2.3 Bonding strength test

According to ISO 4624:1978, a simple and practicable scheme was designed to test the bonding strength between the composite coating and the steel substrate in view of the scratches of the coating, mainly resulting from the effect of shear forces. The bonding strength test of the coating was tested by an HT-2402 universal mechanical testing machine at room temperature. The configuration scheme of the bonding strength test is shown in Figure 1. A thin stainless steel blade with a $\varnothing 2 \text{ mm}$ hole in the center was previously placed on the movable test fixture. The steel wire ($\varnothing 2 \text{ mm}$) with a 2-mm-long composite coating, through a small hole in the middle of the stainless steel blade, was fixed by the test fixtures. The PU

Figure 1: Bonding strength test configuration scheme.

coating with different contents of nano-SiO₂ can be evenly peeled off from the surface of the steel wire by applying a stable force during the test. The displacement rate was 2 mm/min. When the test was finished, the average value was obtained by 10 different samples for each group. The equation was used to calculate the bonding strength between the PU coating and the steel substrate as follows:

$$\sigma = F / A \quad (1)$$

where σ is the bonding strength between the PU coating and the steel substrate (MP), F is the maximum load (N), and A is the area of the PU coating (mm²).

2.2.4 Wear resistance test

According to the wear resistance test by a pin-on-disk test equipment used in the previous research [14], the wear resistance test was carried out by an HT-1000 high-temperature scratch testing machine, using Q235 steel substrate with a size of 50×20×2 mm, with PU coating against a steel bearing ball with a radius of 2.5 mm and a hardness level of HRC62. The applied load was 3 N, the rotation speed of the ball was 400 rpm, and the sliding radius was 5 mm [15]. The equation was used to evaluate the specific wear rate as follows:

$$I = \Delta m / t F \rho \quad (2)$$

where Δm is the loss weight (g), t is the wear time (min), F is the applied load (N), ρ is the coating density (g/cm³), and I is the specific wear rate (cm³/min N).

3 Results and discussion

3.1 Dispersion of nano-SiO₂ in PU

The morphologies of different particles before and after ball milling were studied by SEM as shown in Figure 2. As seen in Figure 2A, the morphology of untreated nano-SiO₂ particles was similar to that of spherical and agglomerated particles partially. It seemed that the dimensions of untreated pure PU particles were not the same, and their edges and angles were sharp as shown in Figure 2B. The magnification of Figure 2C is greater than that of Figure 2B. The surface of the PU particles was not smooth as there were many gaps. The morphologies of PU with different contents of 2 and 5 wt.% nano-SiO₂ after ball milling can be observed in Figure 2D and E, respectively.

It was shown that the edges and angles of PU particles became relatively smooth and nano-SiO₂ particles were adsorbed onto the surfaces of PU particles, so that the combination of organic and inorganic phases was good. A significantly different morphology can be observed in Figure 2F and G, the magnifications of which were greater than that of Figure 2D and E. When the addition of nano-SiO₂ was 2 wt.%, nano-SiO₂ particles were homogeneously distributed onto the surface of the PU particle as shown in Figure 2F. However, when the addition of nano-SiO₂ was 5 wt.%, there were still some agglomerated nano-SiO₂ particles after the process of ball milling (Figure 2G).

One of the reasons for these is that PU particles were pulverized in the process of mechanical ball milling, and their specific surface areas and surface free energies increased. Furthermore, owing to the high specific surface areas and surface free energies of nano-SiO₂ particles [16–18], they were easy to absorb onto the surfaces of PU particles during the process of ball milling. Another reason was that nano-SiO₂ were prone to generating silicon oxygen free radicals and hydrogen radicals in the process of ball milling with PU [19], and then hydrogen bonds were formed between these polar groups and the polar groups of PU, so that nano-SiO₂ was fixed onto the molecular chains of PU. When the content of nano-SiO₂ was 5 wt.%, due to the surface effect and size effect of nano-SiO₂ particles, parts of them were absorbed onto the surfaces of PU particles and the rest of them was not evenly dispersed by reason of agglomeration.

3.2 FTIR spectra of coatings

FTIR spectra were used to characterize the reaction process of nano-SiO₂ and PU during curing. The characteristic peaks of PU can be observed in Figure 3 [11, 20, 21]. The absorption peaks at about 3464, 1712, and 1490 cm⁻¹ were attributed to the stretching vibration of N-H, C=O, and C-N, respectively. The absorption peak at 2270 cm⁻¹ was equivalent to the -NCO groups as shown in Figure 3A.

It can be seen that the absorption peak of the -NCO groups at 2270–2200 cm⁻¹ disappeared in composite coatings with the addition of nano-SiO₂ (compare Figure 3A–C). The reason may be that the -OH groups on the surfaces of nano-SiO₂ particles reacted with the -NCO groups of PU during curing, leading to the decrease of the number of the -NCO groups of PU, so that the absorption peak at 2270 cm⁻¹ in Figure 3A became too weak to detect subsequently in Figure 3B and C. This indicated that nano-SiO₂ particles were grafted to the molecule chains of PU, and a space network structure of organic/inorganic composite was formed.

Figure 2: SEM images of (A) untreated nano-SiO₂, (B and C) untreated pure PU, (D and F) 2 wt.% SiO₂/PU after ball milling, and (E and G) 5 wt.% SiO₂/PU after ball milling.

Figure 3: FTIR spectra of (A) pure PU coating, (B) 2 wt.% SiO₂/PU composite coating, and (C) 5 wt.% SiO₂/PU composite coating.

3.3 Bonding strength

In this work, the bonding strength between the PU coating and the metal substrate was investigated by an HT-2402 universal mechanical testing machine. The stress-strain plots of the PU composite coatings with different contents of nano-SiO₂ is shown in Figure 4. The bonding strength between the composite coating and the metal substrate began to increase and then decreased with the increase of the addition of nano-SiO₂. The bonding strength between the pure PU coating and the metal substrate was 5.26 MPa as shown in Figure 4A. The bonding strength between 2 wt.% SiO₂/PU composite coating and the metal substrate was 7.33 MPa as seen in Figure 4B, which was 39.35% higher than that of the pure PU coating. The bonding strength between 5 wt.% SiO₂/PU composite coating and the metal substrate was 3.97 MPa, which was 24% lower than that of the pure PU (Figure 4C).

When the content of nano-SiO₂ was 2 wt.%, the bonding strength between the composite coating and the metal substrate was better than that of the pure PU coating. The reason may be that hydrogen bonds were generated between the polar groups (such as the -OH groups) of nano-SiO₂ particles and the polar groups (such as the -NCO groups) of PU during the process of ball milling, resulting in an increase of the compatibility between nano-SiO₂ and PU; as a result, it prevented nano-SiO₂ particles from agglomeration [22]. Moreover, the -NCO groups of PU reacted not only with the -OH groups on the surfaces of nano-SiO₂ particles during curing at 200°C but also with the -NHCOO or -CONH groups, leading to the structure of PU coating from linear crosslinking to network crosslinking. Thus, the result may be that the composite

Figure 4: Stress-strain plots of (A) pure PU coating, (B) 2 wt.% SiO₂/PU composite coating, and (C) 5 wt.% SiO₂/PU composite coating.

coating became more compact, and the bonding strength between the composite coating and the metal substrate was improved.

However, when the content of nano-SiO₂ was 5 wt.%, due to the high specific surface areas and surface energies, the number of nano-SiO₂ particles unsuccessfully grafted onto the molecular chains of PU increased and the number of agglomerated nano-SiO₂ particles also increased [22]. Under the action of gravity, parts of the agglomerated nano-SiO₂ particles deposited onto the surfaces of the metal substrate, resulting in the decrease of the contact areas between the PU resin and the metal substrate. Thus, the bonding strength between the PU composite coating and the steel substrate was weakened.

3.4 Wear resistance

The wear rates of the PU coatings are presented in Figure 5. It was found that the wear rates began to decrease and then increased with the increase of the addition of nano-SiO₂, and the optimal addition of nano-SiO₂ was 2 wt.%. The results agreed well with that of the bonding strength test. The wear rate of the pure PU coating was $1.97 \times 10^{-5} \text{ cm}^3/\text{min N}$. The wear rate of 2 wt.% SiO₂/PU composite coating was $1.52 \times 10^{-6} \text{ cm}^3/\text{min N}$, which was 92.28% lower than that of the pure PU coating. The wear rate of 5 wt.% SiO₂/PU composite coating was $3.03 \times 10^{-5} \text{ cm}^3/\text{min N}$, which was higher than that of the pure PU coating.

The lowest value of the wear rate was measured for 2 wt.% SiO₂/PU composite coating. It may be explained as follows. The crosslinking polymerization reaction that occurred between the -NCO groups of PU and other polar

Figure 5: Specific wear rates of SiO₂/PU composite coatings of different weight percentages.

groups during curing at 200°C made the structure of the PU composite coating from linear to network. It led to the result that the composite coating became so compact that it was hard to be worn during friction process. When the content of nano-SiO₂ was 5 wt.%, because the amount of agglomerated nano-SiO₂ particles increased, parts of them were removed onto the track as sliding time goes by, acting as abrasive materials [23], so that the abrasion and breakage of the PU composite coating were intensified, resulting in the increase of the wear rate.

Figure 6 shows the friction coefficient as a function of time for PU coatings with different contents of nano-SiO₂. The friction coefficient of the pure PU coating was 0.42.

Figure 6: Friction coefficient as a function of time for (A) pure PU coating, (B) 2 wt.% SiO₂/PU composite coating, and (C) 5 wt.% SiO₂/PU composite coating.

However, the friction coefficient of 2 wt.% SiO₂/PU composite coating was 0.31, which was 35.48% lower than that of the pure PU coating. The friction coefficient of 5 wt.% SiO₂/PU composite coating was 0.49, which was 16.67% higher than that of the pure PU coating.

It can be concluded that the friction coefficient of the PU coating can be significantly reduced when the addition of nano-SiO₂ was 2 wt.%. The main cause may be that nano-SiO₂ particles were homogeneously dispersed onto the surfaces of PU particles, and a space network structure of the PU composite coating was formed during curing, so that the PU composite coating was more compact and smoother. Therefore, the wear mechanism of 2 wt.% SiO₂/PU composite coating was not abrasive wear but slightly adhesive wear [24]. Additionally, when the content of nano-SiO₂ was excessive, the agglomeration and deposit of nano-SiO₂ particles led to the increase of the friction coefficient and wear rate of the composite coating.

4 Conclusions

In this work, a small amount of nano-SiO₂ particles was added into PU powder by ball milling. After that, a series of PU coatings with different contents of nano-SiO₂ were prepared by electrostatic spraying. When a small amount of nano-SiO₂ particles was added, the -NCO groups of PU reacted with the -OH groups on the surfaces of nano-SiO₂ particles to form a network structure of PU-SiO₂. It greatly improved the wear resistance of the PU coating and its adhesion to the steel substrate. The bonding strength between 2 wt.% SiO₂/PU composite coating and the metal substrate was 7.33 MPa, which was 39.35% higher than that of the pure PU coating. Its wear rate and friction coefficient were $1.52 \times 10^{-6} \text{ cm}^3/\text{min N}$ and 0.31, respectively. Its wear resistance was about 10 times as high as that of the pure PU coating. When an excessive amount of nano-SiO₂ particles was added, the agglomerated nano-SiO₂ particles not only affected the bond between the resin and the steel substrate but also became abrasive materials, intensifying the abrasion and breakage of the PU composite coating during the course of friction. It resulted in lower bonding strength and poorer wear resistance of the PU composite coating. Therefore, the bonding strength between 5 wt.% SiO₂/PU composite coating and the metal substrate was 24% lower than that of the pure PU coating, and its wear resistance was also lower than that of the pure PU coating.

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