Enhancing the Anticorrosion Properties of Waterborne Polyurethane Coatings with SiO_2 Nanoparticles

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Abstract- In this study we attempt to add 3-amino-propyltrimethoxysilane (APTMS) and SiO2 nanoparticles to a waterborne polyurethane (WPU) dispersion to make it an excellent anti-corrosion coating material for protecting metal surfaces. In addition to providing hydrophobicity to the coating, the SiO2 nanoparticles also act as crosslinking points for interconnecting PU chains through reactions with APTMS. In the gel content test, we found that the addition of SiO2 nanoparticles indeed led to a higher degree of crosslinking than the addition of APTMS alone. The degree of crosslinking continued to increase when the concentration of SiO2 was increased from 5 phr to 10 phr. The pencil hardness test and contact angle measurement also showed that increasing the crosslinking degree and SiO2 concentration of the coating can effectively improve the hardness of the coating and enhance its hydrophobicity. The copper sulfate test also revealed that the addition of SiO2 nanoparticles can improve the diffusion resistance of corrosive substances in the coating. Finally, the salt spray test results showed that compared with the coating containing only APTMS, the addition of SiO2 nanoparticles can further improve the corrosion resistance.

Indexed Terms- anticorrosion coating, silane coupling agent, SiO2 nanoparticles, waterborne polyurethane

I. INTRODUCTION

Galvalume steel is a type of coated steel and is widely used in construction, household appliances or computer-related products. It is a carbon steel substrate with an aluminum-zinc alloy coating on the surface [1]. This type of steel has excellent corrosion resistance and a good service life because of the sacrificial anode layer of zinc and the additional dense protective aluminum oxide layer. However, corrosion has always been a major challenge for metal materials. Over time, the aluminum-zinc alloy layer will oxidize and wear out. Therefore, adding an anti-corrosion coating to further passivate the surface can effectively extend the service life of galvalume steel. Polymeric coatings can be used to prevent or reduce corrosion, protecting the galvalume steel substrate from reduced strength and shortened service life due to surface corrosion. This coating can act as a protective barrier between the galvalume steel and the corrosive environment to block the corrosion of moisture, chemicals and other corrosive substances [2]. In addition, polymer films can be easily coated on large areas, the thickness is easy to control, and they are cheap, easy to process and easy to modify to meet different requirements.

Waterborne polyurethane (WPU) is widely used in various fields because of its low volatile organic compound (VOC) emissions. It is not only safe, non-toxic, and environmentally friendly, but also retains the wear resistance and high hardness of traditional polyurethane. The processing process is simple, safe, and low in toxicity. However, compared with traditional polyurethane coatings, their hydrophilic groups lead to disadvantages such as poor water resistance, lower thermal stability, poorer mechanical properties, and long processing cycle. Various modification strategies have been proposed, including chemical grafting of functional groups, cross-linking, and mixing with fillers and even nanomaterials to improve the performance of WPU. SiO2 is the most abundant substance on earth and has a wide range of uses, from glass, ceramics and refractory materials, metallurgy, construction, rubber, plastics, medicine, electronics, coatings. In many studies, it has also been found that adding SiO2 to polymer materials can improve hydrophobicity, hardness, tensile strength, elastic modulus, wear resistance, etc. SiO2 nanoparticles have many advantages in improving coating performance. For example, SiO2 nanoparticles can improve the barrier properties of organic coatings through their hydrophobic properties, lower porosity and increased tortuosity [3, 4]. One of the methods to make SiO2 nanoparticles is to use silane as a precursor. When silane is heated in water, it undergoes hydrolysis and condensation to form a continuous silicon-oxygen Si-O-Si structure. As the water evaporates, a continuous nano-sized three-dimensional SiO2 structure is gradually formed. However, nanoparticles tend to aggregate in WPU liquid mixtures, losing their characteristics and seriously affecting their performance. Surface treatment of nanoparticles, such as selecting silane coupling agents with appropriate functional groups, can enhance the dispersibility of nanoparticles on the one hand, and react with WPU on the other hand to promote the bonding of inorganic nanoparticles and organic polymer matrix, thereby enhancing the adhesion and mechanical strength of nano-SiO2 particle-reinforced WPU. That is, the addition of silane into WPU can improve the anti-corrosion performance of the coating, adding nano-SiO2 can further enhance its thermal stability and hydrophobicity. Therefore, in this study, we added SiO2 nanoparticles and silane to the WPU emulsion. After room temperature solidification and high temperature crosslinking, the Si-OH on the SiO2 particles in the coating formed a continuous hard outer shell with the silane molecules. The other end of the silane molecule is covalently bonded to the WPU molecule to improve the performance of the WPU coating.

II. EXPERIMENTALS

A. Materials

WPU dispersion (solid content 35%, pH 7-9, specific gravity 1 - 1.1, Gabriel Advanced Materials Co.), SiO2 nanoparticle dispersion (40% in Water, 14 nm, Alfa Aesar), APTMS (95%, Thermo Scientific Chemicals), Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, reagent grade, Fluka) were purchased and used as received.

B. Sample Preparation and Characterization

Dilute the received WPU dispersion with DI water from 35% solid content to 15%. Different proportions of silane (APTMS): 3, 5, 8, 10phr, were added into DI water, and after hydrolysis, 5 and 10 phr, respectively, of SiO2 nanoparticle dispersions were added to the respective APTMS mixtures, stirred 5 to 10 min until homogeneous. (1 g of additive was added to 100 g of solid PU for each phr). The two dispersions were then added together and mixed using a magnetic stirrer for about 10 min. The subsequent specimen preparation and characterization methods were the same as those described in [5]. The coating's gel content, hardness, adhesion to galvalume substrates, contact angle, copper sulfate penetration resistance, and salt spray corrosion resistance were all measured.

III. RESULTS AND DISCUSSION

A. Gel content

We have mentioned in [5] that APTMS has the ability to crosslink WPU. Its crosslinking mechanism may be that a condensation reaction occurs simultaneously during hydrolysis. The silane molecules condense into a three-dimensional structure to form crosslinking points. The multifunctional groups on its surface react with PU to crosslink different PU chains together. As can be seen from Figure 1, when SiO2 is added to the WPU/APTMS mixture, APTMS still has a good crosslinking effect. All the data show that the more APTMS is added, the higher the gel content, which indicates, the higher the crosslinking degree. Figure 1 also shows that when APTMS is added at more than 5 phr, the cross-linking effect is significantly improved. However, if we compare the coatings with and without SiO2, we can find that the addition of 5 phr SiO2 does not significantly improve the crosslinking effect. The gel contents of the two types of coatings have similar values. But for the coatings with 10 phr SiO2, the crosslinking degree can be further improved. The gel content values for WPU with only 10 phr of APTMS, with additional 5 phr SiO2 and with additional 10 phr SiO2 are 46.7%, 51.9% and 60.7%, respectively. It is worth noting that after adding SiO2, the coatings with APTMS concentration of 5 phr or higher became extremely brittle.

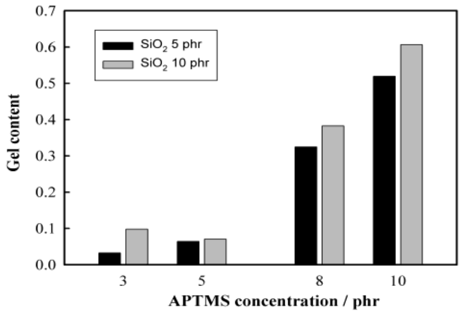

Figure 1. Gel content at different SiO_2 and APTMS concentrations.

B. Tape test and Pencil hardness

Table 1 shows the results of the tape test and the pencil hardness test. In the tape test, 100 lattices were cut on the coating and peeled with a tape. The adhesion was then evaluated by counting the number of the remaining unpeeled lattices. When inorganic SiO2 is added, we expect the adhesion of the resulting WPU coating to the galvalume substrate to be impaired because it has no interaction with the organic WPU matrix or the metal substrate. However, since APTMS effectively facilitated the bonding between SiO2 particles, WPU and metal substrate, all the coatings, even those with high concentration of SiO2, remained intact in the tape test. The pencil hardness test results in Table 1 reveal more about the characteristics of each coating than those of the tape test. The addition of SiO2 nanoparticles significantly increased the hardness of the coatings. For example, for the coatings containing 3 phr APTMS, the hardness value before adding SiO2 was 5B (the softest value in the pencil test is 6B and the hardest value is 6H) [5], and the hardness value increased to B after adding 5 phr SiO2, the value even increased to H when the SiO2 concentration was increased to 10 phr. In addition, increasing the concentration of APTMS can also effectively improve the hardness of the coating, which we also mentioned in [5]. So for the coatings containing 5 phr SiO2, after adding 3, 5, and 8 phr APTMS, their hardness values increased from B to HB and then to H. From Figure 1 we see that the degrees of crosslinking of the coatings containing 3 or 5 phr APTMS are similar and quite low, so the increase in hardness can only be attributed to the increased adhesion contributed by the higher concentration of APTMS. Higher content of SiO2 also helped to improve the hardness of the coating, but the hardness values of the coatings containing 10 phr SiO2 can only reach H, and the higher content of APTMS did not further improve the hardness. Increasing the degree of cross-linking, enhancing the adhesion of the coating to the substrate, and adding hard additives can all help to increase the hardness of the coating, but the addition of nanoparticles does not seem to increase the hardness to the expected extent.

Table 1. The results of tape and pencil hardness tests.

APTMS/SiO_2 concentration (phr)	Tape test*	Pencil hardness
3/5	100	B
5/5	100	HB
8/5	100	H
3/10	100	H
5/10	100	H
8/10	100	H

* The number of the remaining unpeeled lattices.

C. Copper sulfate test and contact angle

The upper graph of Figure 2 shows the times required for copper ions to penetrate the coatings and the aluminum-zinc alloy layer in the copper sulfate test. When aqueous copper ions penetrate the protective layers and undergo redox reaction with the iron of the substrate and replace each other, red copper-brown deposits can be observed. The penetration time helps determine the effectiveness of the coating in resisting moisture and corrosive substances. We can use the penetration times of the coatings without SiO2 as references. The penetration times of the WPU coatings containing 3, 5, and 8 phr of APTMS and without SiO2 is 15, 20, and 25 min respectively [5]. It can be found from Figure 2 that when 5 phr SiO2 were added, the penetration times improved to 20, 25, 30 min, respectively. The improvement must be attributed to the incorporation of SiO2 nanoparticles. We also see improvements for the 3 and 5 phr APTMS coatings when a higher concentration of 10 phr SiO2 is added. We found that the area of the red-brown deposit on the coating containing 8 phr APTMS and 10 phr SiO2 was smaller than that on the coating containing 5 phr SiO2, even though the penetration time of both coatings was the same. Comparing Figure 1 with Figure 2, it can be seen that the increase in penetration time with increasing

APTMS concentration can be attributed to the increase in the degree of crosslinking.

The contact angle of a water droplet can show the degree of hydrophobicity of the coating. The contact angle of the WPU coatings containing 3, 5, and 8 phr of APTMS and without SiO2 is 72.3°, 73.3°, and 74.5°, respectively [5]. From Figure 2, we can see that the contact angle increases when SiO2 is added and the contact angle increases with increasing SiO2 concentration, indicating that the coatings becomes more hydrophobic. The contact angle also increases with increasing APTMS concentration. Among these coatings, the one with the largest contact angle is the one containing 8 phr APTMS and 10 phr SiO2, which is 77.2°. Note that the increase in hydrophobicity does not reach a very high level because APTMS also has a high polarity and the hydrophobic SiO2 nanoparticles are completely covered by the PU polymer chains and the structures formed by the condensation of APTMS molecules.

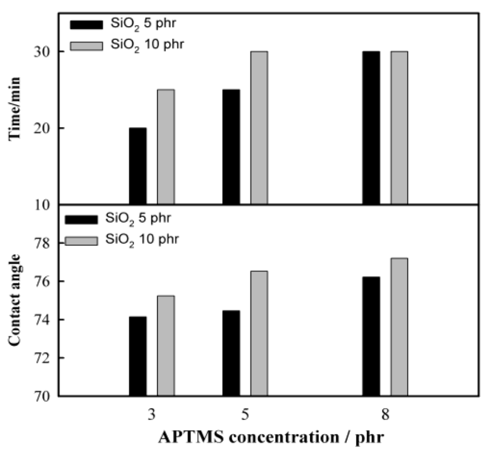

Figure 2. Copper ion penetration time and contact angle at different SiO_2 and APTMS concentrations.

D. Salt spray test

Salt spray test can best show the ultimate protective effect of various coatings on galvalume steel. Figure 3 shows the surface of galvalume steel sheets with different WPU coatings after 72 h of testing. For the coating containing 3 or 5 phr APTMS and without SiO2, obvious black spots appeared at 24 h of testing. However, for the coating containing additional 5 phr or 10 phr SiO2, the black spots were not apparent at 24 h, but only appeared clearly at 48 h. For the coating with 8 phr APTMS added but without SiO2, its behavior was similar to the coatings with 3 and 5 phr APTMS added but without SiO2, and black spots also appeared at 24 h, but to a lesser extent. When adding 5 phr SiO2 to the coating, black spots were only apparent at 48 h. When 10 phr SiO2 was added to the coating, black spots only appeared at 72 h. As shown in Figure 3, after 72 h of salt spray test, the coatings with 3 phr APTMS showed some areas of rust, but the coating with 10 phr SiO2 were less serious. For coatings containing 5 or 8 phr APTMS, after adding 5 or 10 phr SiO2, the pictures of the galvalume steel sheets shown in Figure 3 are very similar, and the rust spots are not obvious. The addition of SiO2 greatly improves the corrosion resistance of the WPU coating through their hydrophobicity and increased tortuosity.

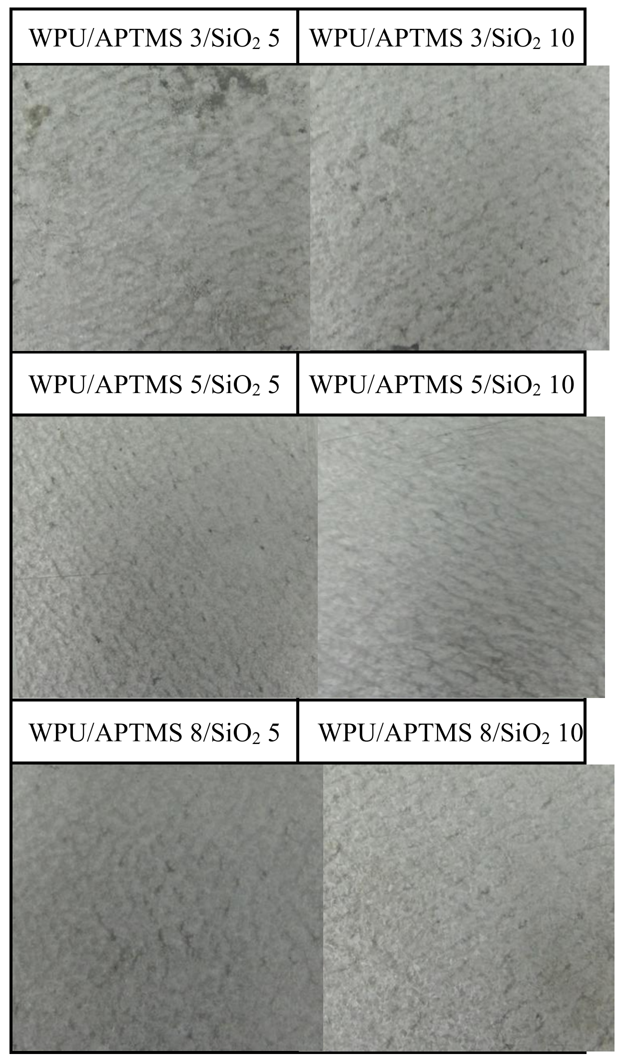

Figure 3. Results of salt spray test at 72 h.

REFERENCES

[1] S. P. Yu, H. J. Tai, ―Sol-gel enhanced polyurethane coating for corrosion protection of 55% Al-Zn alloy-coated steel, J. Polym. Res., vol. 28, article 158, 2021.

[2] I. I. Udoh, O. O. Ekerenam, E. F. Daniel, A. I. Ikeuba, D. I. Njoku, S. K. Kolawole, I. N. Etim, W. Emori, C. N. Njoku, I. P. Etim, P. C. Uzoma, ―Developments in anticorrosive organic coatings modulated by nano/microcontainers with porous matrices, Adv. Colloid Interface Sci., vol. 330, article 10329, 2024.

[3] F. B. Liu, J. B. Liu, Y. N. Zhang, J. Y. Zhu ―Improvement of the long-term corrosion resistance and adhesion property of waterborne polyurethane coatings by physical mixing with silane-grafted nano-SiO2/TiO2, Surf. Interfaces, vol. 56, article 105709, 2025.

[4] J. Gąsiorek, A. Gąsiorek, B. Babiarczuk, W. Jones, W. Simka, J. Detyna, J. Kaleta, J. Krzak, ―Nanocomposite organic coatings for corrosion protection of metals: A review of recent advances, Prog. Org. Coat., vol. 162, article 106573, 2022.

[5] H. J. Tai, H. S. Hsieh, ―Anticorrosion properties of waterbrone polyurethane/3-aminopropyltrimethoxysilane coatings, IRE Journals, vol. 8, no.1, pp. 9-13, 2024.