Anticorrosion Properties of Waterbrone Polyurethane/3-aminopropyltrimethoxysilane Coatings

HORNG-JER TAI[1], HSIN-SHENG HSIEH[2]
Institute of Biotechnology and Chemical engineering, I-Shou University

Abstract- In this study, we introduced different doses of silane coupling agent: 3-amino-propyltrimethoxysilane (APTMS) into commercial waterborne polyurethane (WPU) to prepare anti-corrosion coatings on galvanized steel sheets and explore their protective properties. In the gel content test, it was found that as the concentration of APTMS reached to higher than 5 phr, the degree of crosslinking was effectively increased. In the tape test, we found that the adhesion of all these WPU coatings passed the specifications. The pencil hardness test results show that the hardness of the coating also increased with the increase in APTMS concentration due to the increase in crosslinking degree. The copper sulfate test results show the same trend as the hardness test that the resistance to aqueous copper ions penetration increased with increased APTMS concentration. The contact angle test results show that the coating hydrophobicity increased with the APTMS concentration. Finally, the salt spray test results show that increasing the APTMS concentration could continuously improve the corrosion resistance of the coating within the concentration range of 8 phr.

Indexed Terms- Corrosion Protective Coating, Crosslink, Silane Coupling Agent, Waterborne Polyurethane

I. INTRODUCTION

Polyurethanes (PUs) are one of the most versatile polymers. Since their production in 1952, a lot of effort has been devoted to their research and development. They are now widely used in adhesives, pipes, foamed plastics, medical materials, coatings, etc. In recent years, environmental awareness has led governments to impose many regulatory restrictions on volatile organic compounds. Accordingly, the application of more environmentally friendly waterborne polyurethane, WPU, has become more popular. In terms of production, WPUs are not only safe, non-flammable, non-toxic and do not pollute the environment, but also retain the wear resistance and high hardness of traditional polyurethanes [1]. Moreover, they are easy to modify and process. WPUs have begun to be used in coatings and wood adhesives, leather industry, textiles, automobile industry, rubber products, etc. However, WPUs still have some properties that are inferior to traditional PUs. In order to make WPUs' thermal stability, moisture resistance, and mechanical properties comparable to traditional PUs, many methods have been proposed to improve various aspects of WPUs' properties.

The steel industry is the foundation of modern development and has extensive industrial connections, driving the development of upstream transportation, mining, and downstream construction, various infrastructure developments, metal products, automobiles, electrical appliances and other related industries. Corrosion prevention is a very important issue for the steel industry. Among many anti-corrosion technologies, polymer coatings are also competitive in the large-scale steel industry. Polymer films can not only be coated on large areas with excellent thickness precision, but they are also wear-resistant and high-strength, cheap, easy to process, and easy to be modified to achieve the different desired performance requirements. PU coating, which has excellent adhesion and weather resistance, is commonly used as the anti-corrosion coating for steels. For environmental reasons, the new WPU coating process is gradually replacing traditional PU coating process. WPU can be divided into [2]: (1) PU aqueous solutions: transparent, particle size < 1 nm; (2) PU dispersions: translucent, particle size 1 ~ 100 m; (3) PU emulsions: opaque, particle size > 100 nm. Of the three, WPU dispersion is the most common. When a polymer dispersion is coated on a substrate, the water will evaporate over time and the particles will gradually become closer. When the temperature exceeds the minimum film formation temperature, the boundaries between the particles will gradually disappear and eventually a film with uniform density forms. Organosilanes are often added to WPU to improve adhesion, thermal stability, and water resistance [3]. The functionalization of organosilanes comes from the interaction with water. When silane comes into contact with water, hydrolysis occurs, forming silanol groups. When heated in a coating process, the silanol groups are further hydrolyzed and subsequently dehydrated and condensed to form a continuous three-dimensional network structure. This network structure reacts with the hydroxyl groups on the metal surface and is covalently connected to the metal substrate, thereby enhancing the overall performance of the coating. The properties of the final coating vary with hydrolysis conditions such as pH value, temperature, reactant ratio, solvent composition, etc. [4] In this study, we used a commercially available WPU and added a coupling agent 3-aminopropyltrimethoxysilane, APTMS, to coat the surface of a commonly used galvanized steel sheet to form an anti-corrosion protective film. Combined with tests such as gel content, adhesion, hardness, contact angle, copper sulfate, and salt spray, we would like to understand the various properties of the modified WPU coatings.

II. EXPERIMENTALS

A. Materials

WPU dispersions (solid content 35%, pH 7-9, specific gravity 1 - 1.1, Gabriel Advanced Materials Co.), APTMS (95%, Thermo Scientific Chemicals), Sodium Chloride (NaCl, reagent grade, Merck), Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, reagent grade, Fluka) were purchased and used as received.

B. Sample Preparation

Mix the received WPU with DI water to prepare a WPU dispersion with a solid content of 15%. Take a certain amount of APTMS, add it into DI Water to hydrolyze it, and mix it with the WPU dispersion under magnetic stirrer for 10 min to make 3, 5, 8, and 10 phr mixtures respectively (1 g of APTMS was added to 100 g of solid PU for each phr). The mixtures were poured into rectangular polypropylene molds and air-dried at room temperature for 5 to 7 days. The solidified films were then placed in an oven and slowly heated for 1 h by increasing the temperature from room temperature to 150°C for crosslinking.

C. Characterization and Testing

The gel content of the crosslinked WPU samples were measured by a reflux extraction method. The sample was placed in a homemade stainless wire mesh pouch and immersed in boiling acetone for 24 hours. The gel content is the ratio of the remaining gel weight to the original sample weight. Adhesion between the WPU/ATPMS coatings and the galvanized steel sheet was evaluated using the tape test specified in ASTM D3359. The WPU/ATPMS dispersion was coated on the surface of the galvanized steel sheet by spin coating, and the rotation speed and time were controlled to achieve a coating thickness of approximately 10 µm. The coating was then cured at 150 °C for 1 h. 100 perpendicular lattices were cut through the coated film to the surface of the galvanized steel substrate and 3M tape was applied over the lattice and then removed. The adhesion was then evaluated by inspecting the grid area for removal of coating and counting the number of the remaining unpeeled lattices. The coating hardness was measured by the pencil test specified in ASTM D3363. The WPU/ATPMS dispersion was coated on a glass plate and crosslinked at 150 °C for 1 h. A pencil of known hardness was mounted on a standard tester under a specified load and at an angle of 45° to the coated glass plate. After pushing the tester forward at a fixed speed for a distance of 3 to 5 cm, the surface was inspected for scratches or gouges. The order of pencil hardness values in the above procedure was (softest to hardest) 6B, 5B, 4B, 3B, 2B, B, HB, H, 2H, 3H, 4H, 5H, 6H and 3 tests were performed for each hardness value. The hardness was determined as the hardness value of the hardest pencil which did not scratch the coating. To test the passivation effectiveness of the coatings, copper sulphate test was performed. When copper sulfate solution penetrates the coating and comes into contact with free iron, the dissolved copper ions precipitate due to redox reactions. Red copper deposit can be observed on the passivated steel substrate if the coating failed to protect it. The test began with dividing the surface of the WPU/ATPMS coated galvanized steel sheet into 12 grids with a pen. After dripping these 12 grids individually with a fixed amount of copper sulfate solution, wiped off the solution one grid after another every 5 minutes and observed the changes. It totally took 1 h for each specimen. Another test taken to evaluate the passivation effectiveness of the coatings was contact angle measurement. Moisture resistance can be determined using the pendant drop method by measuring the contact angle between a water droplet and the coatings. A Dataphysics OCA20 instrument was used for the measurements. To further evaluate the corrosion resistance of the coatings, a Weiss SC450 corrosion and salt spray test chamber was used to conduct salt spray tests. Salt spray testing is an environmental test that mainly uses a controlled saline environment to evaluate the corrosion resistance of metal materials at an accelerated rate. This test uses a 35°C, 5% sodium chloride aqueous solution, which is atomized and sprayed in a fixed humidity chamber. The test specimens are exposed in the high-salinity environment and corrodes at an accelerated rate. It can simulate in one day a real corrosion process that would take one year in a natural environment.

III. RESULTS AND DISCUSSION

A. Gel content

It can be seen from Figure 1 that when APTMS is introduced, WPU can be effectively crosslinked. As the APTMS concentration increases, the cross-linking degree increases, and the gel content increases from 0% at 0 phr to 46.71% at 10 phr. During the film casting process, it was found that APTMS was easy to hydrolyze with water molecules, and this reaction did not take a long time. When the crosslinking degree of WPU increased, the hardness and water resistance would theoretically increase. The gel content of WPU increased significantly after the concentration of APTMS exceeded 3 phr. In addition, as the concentration of APTMS increased, the overall flexibility of the films decreased and the films became very hard and brittle. The change started with an APTMS concentration of 8 phr.

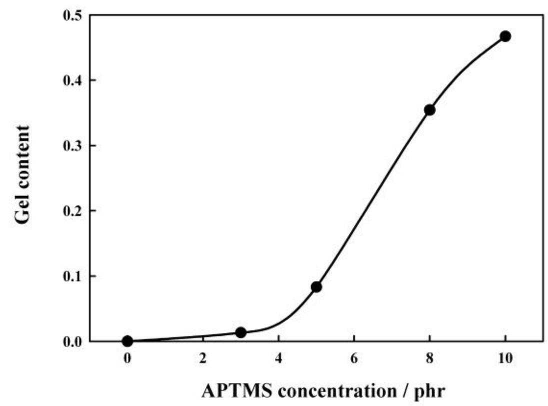

Figure 1. Gel content vs. APTMS concentration.

B. Tape test and Pencil hardness

The tape test result is shown in Table 1. Theoretically, the dispersion added with APTMS will form covalent bonds with the surface of the steel sheet, thereby improving the adhesion. However, in the test, all values for the remaining unpeeled lattices number, including that for pure WPU dispersion, were 100, indicating that no peeling was detected visually. The function of APTMS cannot be seen in this test. At least, it shows that the coatings made here had good adhesion with the surface of the galvanized steel sheet, and could pass this test perfectly. In the pencil hardness test result, shown also in Table 1, we can see clearly that the hardness of the coatings, as more APTMS is added, increases from 6B for pure WPU to HB for WPU with 8 phr of APTMS. We see that the hardness values increase the most when the concentration of APTMS increases from 3 phr to 5 phr, which is closely related to the large increase in the degree of crosslinking (see Figure 1). It was mentioned in the previous discussion that with the introduction of APTMS, both the crosslinking degree of the film and the number of chemical bonds between the coating and the surface of the steel sheet will also increase. The flexibility of the material will decrease and the rigidity will increase, so the hardness of the film will increase.

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

APTMS concentration (phr)	Tape test*	Pencil hardness
0	100	6B
3	100	5B
5	100	B
8	100	HB

* The number of the remaining unpeeled lattices.

C. Copper sulfate test and contact angle

The copper sulfate test can be used to determine the effectiveness of a coating's corrosion resistance. The longer it takes for reddish-brown deposits to form on the galvanized steel sheet, the better its corrosion resistance. It can be found from Figure 2 that when APTMS is added with only 3 phr, its corrosion protection capability is only equivalent to that of pure WPU. It only took 15 min for copper sulfate to penetrate through the two coatings and reacted with steel iron. From Figure 1, we know that

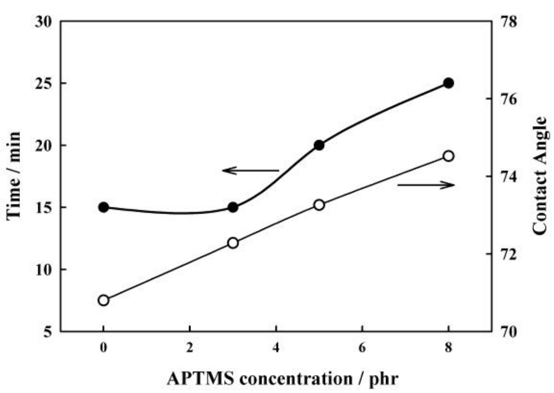

Figure 2. Copper ion penetration time and contact angle vs. APTMS concentration.

the crosslinking degree of the coating containing 3 phr APTMS is very low, so its resistance to the penetration of aqueous copper ions is very low. In comparison, when the APTMS concentration increased to 5 and 8 phr respectively, the time for red-brown deposits to appear on the steel surface became 20 and 25 min respectively, and the corrosion resistance was significantly improved. The higher degree of crosslinking of the coating made it more difficult for copper ions to penetrate the protective coating and react with surface iron. It can also be seen in Figure 2 that the contact angle of the coating increases as the concentration of APTMS increases, and the increase in contact angle represents an increase in the hydrophobicity of the coating. Increased hydrophobicity also helps improve the moisture resistance of the coating.

D. Salt spray test

In the experiment, it was found that the steel sheet coated with pure WPU dispersion corroded severely under salt spray at 24 h. Obvious white rust and large black corroded areas also appeared on the subsequent 48 h and 72 h specimen surfaces. With the introduction of APTMS, the corrosion protection capability of the coatings began to appear. When coated with the WPU dispersion containing 3 phr APTMS, black spots still appeared on the steel sheet surface at 24 hours, but there was a significant improvement compared to the pure WPU coating. At 72 h, as shown in Figure 3, some obvious traces of black rust were visible, but there was no white rust. For the specimen coated with the dispersion containing 5 phr APTMS, the black rust marks area was even smaller at 72 h. Finally, for the specimen coated with the dispersion containing 8 phr APTMS, the improvement was more obvious, and only a few tiny black rust spots were observed at 72 h. The addition of APTMS greatly improves the corrosion resistance of the WPU coating by increasing the crosslinking degree of the coating and promoting adhesion to galvanized steel sheets.

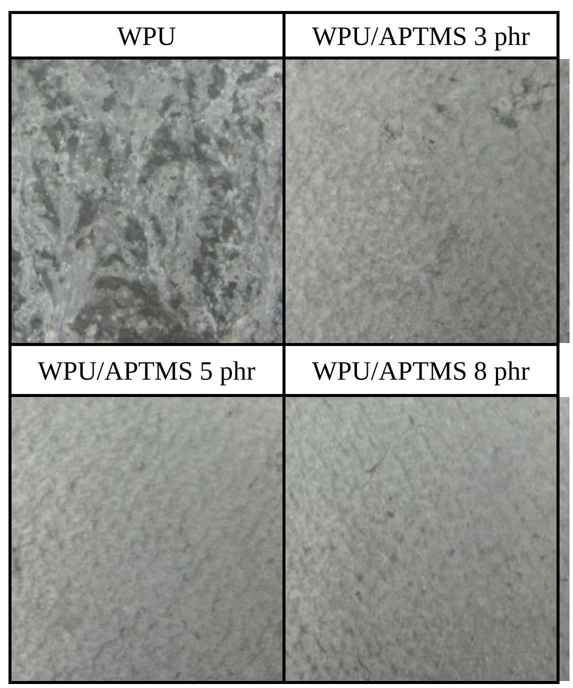

Figure 3. Results of salt spray test at 72 h.

REFERENCES

[1] H. Honarkar, ―Waterborne polyurethanes: A review, J. Dispers. Sci. Techno., vol. 39, no. 4, pp. 507-516, 2018.

[2] A. Patti, D. Acierno, ―Structure-property relationships of waterborne polyurethane (WPU) in aqueous formulations, J. Vinyl Addit. Technol., vol. 29, no. 4, pp. 589-606, 2023.

[3] J. Li, L. Zhao, C. Hong, M. Liu, Y. Wang, Y, Song, R. Zhai, J. Zhang, C. Zhou, ―Synthesis and characterization of waterborne polyurethane-based ink binder modified via a silane coupling agent, Prog. Org. Coat., vol. 186, article 108018, 2024.

[4] J. Gąsiorek, A. Gąsiorek, B. Babiarczuk, W. Jones, W. Simka, J. Detyna, J. Kaleta, J. Krzak, ―Anticorrosion properties of silica-based sol-gel coatings on steel – The influence of hydrolysis and condensation conditions, Ceram. Int., vol. 48, no. 24, pp. 37150-37163, 2022.