Synthesis and corrosion Resistance of silane coupling agent modified graphene oxide/waterborne polyurethane

S S Shu1, L Wu1,2, J M Liu1, Y Liu1, Y Hu1,2, J H Xu1 and L Wang1

1Research Institute of Applied Chemistry, Wuhan University of Science and Technology, Wuhan 430081, China
2Academy of Green Manufacturing Engineering, Wuhan University of Science and Technology, Wuhan, 430081, China

Corresponding Author: Wu Lin E-mail address: wulin@wust.edu.cn

Abstract. In this paper, graphene oxide (GO) is used as a matrix, and it is modified with a silane coupling agent (KH550) to prepare modified GO. The GO/waterborne polyurethane composite coatings with different contents are prepared by chemical grafting, and their structural characterization tests are carried out. The results show that the silane coupling agent can effectively modify GO, and the surface of the modified GO has more oxygen-containing functional groups. The added modified GO can effectively enhance the corrosion resistance of the coating, and the corrosion resistance of the composite coating was optimal when the mass fraction is 0.03%, and 5% corrosion occurs after 48 h, and the total corrosion time reaches 120h.

1. Introduction
The waterborne urethane oligomer is synthesized by using polyether diol and isophorone diisocyanate as the main raw materials, and utilizing oxygen-containing functional groups on the graphene oxide (GO), such as hydroxyl and epoxy functional groups and -NCO groups in the diisocyanate. A chemical reaction occurs and is linked to the GO by a covalent bond. In order to improve the dispersibility of GO in the waterborne polyurethane (WPU) matrix and significantly improve the transport and fluidity of the particles in the GO/WPU composite, it is necessary to functionally modify the GO in actual production. Silicon has the advantage of being cheap and easy to obtain. Therefore, silane coupling agents, polysiloxanes, and nano-silicon materials are often used as modifiers for GO to improve their properties, so that the composites exhibit good durability and plasticity.

2. Experiment

2.1. Preparation of modified GO
400 mg of GO was weighed and added to a beaker containing 80 mL of deionized water, and ultrasonically dispersed for 2 h to obtain a GO dispersion having a concentration of 5 mg/mL. 4 g of a silane coupling agent (KH550) was weighed into a beaker, and all of it was dissolved by adding a certain amount of absolute ethanol. The prepared GO dispersion was added to the beaker and ultrasonically dispersed for 30 min. Adjusted the pH of the system to 4-5 with 0.1 mol/L hydrochloric acid. After dispersion, the solution was heated to 50 °C under low-speed stirring for 30 min, then the temperature was raised to 70 °C for 2 h. After the completion of the reaction, the mixture was washed...
3-4 times by centrifugation, and the precipitate was dried at 60 °C for 12 h to obtain a modified GO powder.

2.2. Preparation of GO/WPU composite emulsion
A certain amount of modified GO was weighed into a beaker containing 21 mL of polyether glycol, which was ultrasonically dispersed for 30 min. Then transferred it to a four-necked flask; added 12 mL of isophorone diisocyanate (IPDI); stirred to 50 °C for 30 min; then warmed to 80 °C for 2 h; weighed 2 g of 2,2-bis (hydroxymethyl) propionic acid (DMPA), dissolved in a small amount of NMP, added to a four-necked flask, and reacted at 80 °C for 4 h. A 1 g sample was taken to titrate the amount of remaining -NCO to determine the amount of ethylenediamine. The four-neck flask system was cooled to 30 °C and a certain amount of acetone was added to reduce the viscosity of the system. Adding triethylamine to neutralize salt formation reaction for 0.5 h; adding metered ethylenediamine for 0.5 h. The GO/WPU emulsion having a solid content of 35% was obtained by adding a deionized water at a constant rate with a constant pressure water separator at a stirring speed of 2500 r/min for 15 min.

2.3. Structure Characterization

2.3.1. Fourier transform infrared spectroscopy (FT-IR). Take 1-2 g of modified phenolic resin in a 50mL tube and add a small amount of ethylene glycol to dissolve. The KBr sheet is compressed by spectral pure KBr tabletting method, and then a small amount of the dissolved sample is coated on the disposable pipette, and then subjected to infrared spectrum detection, and the scanning range is 400-4000 cm⁻¹.

2.3.2. Scanning electron microscope (SEM). A block of carbonized product of appropriate size is placed on the sample stage, and the sample is prepared and subjected to gold spray treatment, and then place it in an instrument to observe the microstructure.

2.3.3. Lead acetate test. Three drops of a 0.5% lead acetate solution are uniformly dropped onto the cured galvanized sheet coating to observe the blackening and complete blackening time of the galvanized sheet.

2.3.4. Salt spray resistance test. Put the galvanized sheet into the neutral salt spray test chamber; set the test temperature to 37 °C, the pressure temperature to 47 °C, and spray continuously. Observe the corrosion of the galvanized sheet at regular intervals.

3. Results and discussion

3.1. Infrared spectroscopy (FT-IR) analysis

![FT-IR spectrum of GO, modified GO samples](Image)

Figure 1 FT-IR spectrum of GO, modified GO samples
Figure 1 is an infrared spectrum of GO and modified GO. GO has a distinct -OH stretching vibration peak (3454 cm⁻¹), a strong C=O stretching vibration peak (1645 cm⁻¹), and a C-O-C bond stretching vibration peak (1113 cm⁻¹). All indicate that there are many oxygen-containing functional groups on the GO. The modified GO shows a new peak near 3000 cm⁻¹, and its wavelength range is -CH₃ and -CH₂ in the silane coupling agent, indicating that KH550 successfully react with GO. In addition, a new strong peak appears in the vicinity of 1000 cm⁻¹, such as the peak at 1097 cm⁻¹ and 1041 cm⁻¹, which is formed by the stretching vibration of Si-O-C and Si-O-Si bonds. The modified GO is successfully formed by GO and the silane coupling agent.

Figure 2 FT-IR spectrum of WPU, GO/WPU samples

Figure 2 is an infrared spectrum of WPU, modified GO/WPU. Seen from figure 2, 1014 cm⁻¹, 1105 cm⁻¹, 1251 cm⁻¹, 1458 cm⁻¹ as the characteristic peaks of the WPU. Therefore, the addition of the modified GO does not affect the general trend of the infrared spectrum of the WPU (the presence or absence of the absorption peak), but only affects the width and sharpness of the absorption peak. It can be seen from the figure that the water-based polyurethane composite material after the addition of the modified GO has a broader and sharper peak formed by stretching vibration of an oxygen-containing functional group such as a hydroxyl group, a carboxyl group or a carbonyl group. It can be concluded that GO carries a rich surface of oxygen-containing functional groups and is successfully grafted onto the WPU.

3.2. Scanning electron microscopy (SEM) analysis

Figure 3 SEM spectrum of WPU sample and 0.03%GO/ WPU

Figure 3 is a scanning electron micrograph of pure WPU. Figure 3 is a 5000-fold magnification of a water-based polyurethane film. It can be found that there are unevenly distributed white spots,
indicating that the pure WPU coating has many defects, and of course it has a smooth and pure appearance. On the right is a scanning electron micrograph of a modified GO/WPU composite film magnified 5000 times. It can be clearly seen that the surface of the composite coating is smooth and smooth, and is purer than the former without any white spots. It can be indicated that the addition of modified GO can help to improve the defects of WPU film, and the preparation of composite materials is successful. Due to the special small size effect of the modified graphene, the pores of the WPU coating can be effectively filled, the density of the coating is increased, and the corrosion resistance of the composite is improved. At the same time, due to the presence of rich oxygen-containing functional groups on the surface of the modified GO, a stable bond can be formed with the WPU by covalent bonding, which greatly increases the adhesion of the composite coating and increases the composite material.

3.3. Lead acetate test

The results of lead acetate titration are as follows:

| time (s) | WPU | 0.03%GO/WPU | 0.05%GO/WPU | 0.1%GO/WPU | 0.15%GO/WPU | Blank plate |
|---------|-----|-------------|-------------|------------|-------------|-------------|
| Black appears | >300 | >300 | >300 | >300 | >300 | 1 |
| Completely blackened | >300 | >300 | >300 | >300 | >300 | 2 |

Compared with the blank plate, the coatings showed no significant change over a long period of time, which proved that the polyurethane coating had certain insulation and anti-corrosion properties.

3.4. Analysis of neutral salt spray test

Salt spray test statistics are as follows:

| time (h) | Blank plate | WPU | 0.03%GO/WPU | 0.05%GO/WPU | 0.1%GO/WPU | 0.15%GO/WPU |
|---------|-------------|-----|-------------|-------------|------------|-------------|
| Start corrosion | 1 | 8 | 12 | 10 | 10 | 14 |
| 5% white rust | 2 | 24 | 48 | 35 | 30 | 33 |
| All white rust | 4 | 55 | 120 | 90 | 78 | 48 |

It can be seen from the above table 2 that the WPU composite containing 0.03% modified GO has the best corrosion resistance, the 5% white rust appearance time is 48h, and the total corrosion is 120 h. The initial corrosion time of 0.15% modified GO/WPU is 14 h. The reason may be that the modified GO is added too much, and some of the GO not participating in the reaction is filled into the void of the WPU by physical mixing. It has enhanced its water resistance, so the corrosion resistance is better than the former. After a period of time, because the adhesion performance is not as good as the former, the film peels off faster and there is a faster corrosion. It can be seen from the test that the WPU film of 0.03% modified GO still does not fall off after 90 h. After 120 h, although the film is foamed, the area of the substrate is still intact, and it can be explained that the addition amount of the modified graphene oxide should be about 0.03%.

4. Conclusion

The KH550 can effectively modify the GO. The infrared spectrum of the sample shows that the surface of the modified GO has more oxygen-containing functional groups than the graphite oxide, and it can be more effectively linked to the WPU by covalent bonding. The addition of modified GO can enhance the corrosion resistance of WPU, but the enhancement range is related to the addition content of modified GO. The neutral salt spray test shows that the optimum addition amount of modified GO is 0.03%, and the corrosion area within 48 h does not exceed 5%.
Reference

[1] Ye Q X 2017 Chemical propellant and polymer materials. 15 1-10
[2] Lu S H, Lei Y, Zhu L L and Li N G 2018 Journal of Shaanxi University of Science and Technology. 36 135-41+52
[3] Di Credico B, Levi M and Turri S 2013 Eur Polym J. 49 2467-76
[4] Hu J, Li X J, Zhang F, Sun D X and Zhang Y H 2015 Polymer Science and Engineering. 31 163-8
[5] Zhao L, Chen Y X, Wang T and Wu L G 2015 Journal of Composite Materials. 32 673-82
[6] Li H 2018 Chemistry and Bonding. 40 351-4
[7] Wang H R, Wang X and Zhao X Y 2018 Applied Chemicals. 47 218-20+5
[8] Yang Z H, Du Y W, Chen R, Liang C and Wu G F 2017 Journal of Materials Protection. 50 61-4
[9] Zhou C F 2014 Shanghai Plastics. 1 1-8.
[10] Xu J K, Xin M H, Li M C and Liu X G 2018 Journal of Huaqiao University (Natural Science). 39 7-15.
[11] Zheng Y, Hu P, Zhang X, Huang Z X, Li K and Huang Z H 2018 Functional Materials. 49 217-21.
[12] Zhang J S, Zhang Y, Li H, Shi Y, Lin R Q and Zhou C 2018 Polyurethane Industry. 33 43-6.
[13] Xu W Z, Zhang B L, Nie Z T, Li A J, Xu B L and Xia L Y 2016 New Chemical Materials. 5 70-3.
[14] Chen Z , Lu H 2012 J Mater Chem. 22 12479.
[15] Kumar M, Chung J S, Kong B S, Kim E J and Hur S H 2013 Mater Lett. 106 319-21.