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Study on preparation and corrosion resistance of graphene oxide modified polyurethane resin

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Abstract. In this paper, isophorone diisocyanate is used to modified with graphene oxide, in which the isocyanate group can react with the oxygen-containing functional group in the graphene oxide. Then we can obtain the modified graphene oxide, thereby allowing the occurrence of grafting reaction on the graphene oxide and the polyurethane resin. Scanning electron microscopy, Fourier transform infrared spectroscopy, neutral salt spray test and electrochemical test are used to characterize the structure and properties of the modified graphene oxide and polyurethane coatings.

1. Introduction

Graphene oxide and graphene have many similarities in structure and properties, such as two-dimensional layered planar structures^[1-3]. Therefore, similar to graphene, functional groups on the surface of graphene oxide can react with polymers to form strong chemical bonds, or can be combined with polymers as fillers^[4-8]. In combination with polymer materials, many properties of raw materials can be greatly improved. Through this feature, graphene can be widely used in electrodes, engineering materials, coatings, and other related fields^[9-12].

2. Experiment

2.1. Preparation of Modified Graphene Oxide

200 mg of GO and 20 mL of N,N-dimethylformamide (DMF) are added to the round-bottomed flask, followed by ultrasonic dispersion for 2 h to obtain a uniformly dispersed GO suspension; 2.0 g of isofluoride is added to the GO suspension. The ketone diisocyanate is stirred under the protection of N2 for 24 h. The obtained product is washed with DMF and dichloromethane for 2 to 3 times. And functionalized graphene oxide can be obtained by drying at 40 $^{\circ}$ C.

2.2. Preparation of Graphene Oxide Modified Polyurethane Resin (IP-GO/WPU) Composite Emulsion

The certain mass fraction of IP-GO is added to 20 mL of DMF and dispersed ultrasonically for 2

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h.The uniformly dispersed IP-GO is added to the WPU and mixed well. After mechanical stirring for 4 h, the mixture is allowed to stand for 2 min to remove the bubbles in the mixture. Then different amounts of IP-GO/WPU composite emulsion are obtained.

According to the above steps, the polyurethane composite emulsion having IP-GO contents of 0.1 wt%, 0.2 wt%, 0.3 wt%, 0.4 wt%, 0.5 wt% and 1.0 wt% are prepared.

2.3. Preparation of composite coatings

Pure polyurethane emulsions and modified polyurethane composite emulsions containing functional GO with different mass fractions are evenly coated on galvanized plates. Ask a sample to apply 3 galvanized plates for more accurate experimental data. Then they are placed in a vacuum oven at 60° C for 2 hours to give the polyurethane coating.

3. Results and discussion

3.1. Analysis of SEM test results

Figure 1 shows SEM images of GO and IP-GO at 20000x. It can be seen from the topography of graphene oxide in figure 1(a) that GO surface is smooth and has a large specific surface area. As shown in figure 1(b), the functionalized GO after modification shows a large change in morphology, showing clusters between the molecules, indicating that the added isophorone diisocyanate had reacted with GO.



Figure 1. SEM Images of GO and IP-GO Samples: (a) GO, (b) IP-GO.



Figure 2. The SEM image of Galvanized sheet sample: (a) Substrate, (b) Prepared coating. Figure 2 is an SEM image of the substrate and the prepared coating. From figure 2, it can be seen that the surface of the substrate is not even while the prepared coating has a smooth surface and is

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completely covered with no solid particles and deposits.

3.2. Fourier infrared spectroscopy

As shown in figure 3, the infrared spectra of IP-GO and GO are shown from top to bottom. GO has a pronounced -OH stretching peak (3454 cm^{-1}), a strong C=O stretching peak (1645 cm^{-1}), and a C-O-C bond stretching peak (1113 cm^{-1}). All of these indicate that there are many oxygen-containing functional groups on GO; for the modified GO, the absorption peak area of -OH stretching vibration (3454 cm^{-1}) is significantly reduced, which indicates that The NCO group on the added IPDI successfully reacted with the oxygen-containing functional group on GO, and there also is a strong C=O stretching vibration peak (1645 cm^{-1}) and a C-O-C stretching vibration peak (1113 cm^{-1}) on IP-GO.



Figure 3. Infrared spectra of GO and IP-GO samples.

Figure 4 shows the infrared spectra of WPU and graphene oxide modified WPU. The ordinary WPU has obvious NH stretching vibration peak (3592 cm⁻¹) and C=O stretching vibration peak (1739 cm⁻¹) on the urethane bond, of which 1530 cm⁻¹,1391 cm⁻¹,1242 cm⁻¹,1094 cm⁻¹ is the four characteristic absorption peaks on the polyurethane molecular chain. The modified WPU had a pronounced -OH stretching peak (3462 cm⁻¹), and the stretching vibration peak at the alkyl group (2937 cm⁻¹, 2878 cm⁻¹) is significantly enhanced. At the same time, a new N-C=N stretching vibration peak appears at 1659 cm⁻¹, which indicate that the amino group on IP-GO reacted with the nitrile group on the polyurethane. And IP-GO successfully reacted with polyurethane.



Figure 4. Infrared spectra of pure WPU and IP-GO with a content of 0.5 wt%.

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3.3. Neutral salt spray corrosion test

The corrosion at 72 h is shown in figure 5. With the increase of the IP-GO content, the corrosion area of the galvanized sheet gradually decreases. When the content exceeds 0.3 wt%, the corrosion area of the galvanized sheet begins to increase. The corrosion area of the blank group has reached more than 80%, while the corrosion area of the galvanized sheet with an IP-GO content of 0.3% by weight is less than 5%, and the corrosion area is the smallest. In summary, when the IP-GO content is 0.3 wt%, the polyurethane resin coating works best, and the corrosion area at 72 h is less than 5%.



Figure 5. Corrosion of galvanized sheet 72h.

3.4. Electrochemical testing

3.4.1 Polarization Curve Analysis

The measured polarization curve is shown in Figure 6. As can be seen from the figure, the corrosion potential of the polyurethane coating with an IP-GO content of 0.3% by weight is positively shifted compared to the untreated substrate. It shows that the polyurethane coating inhibits the entire electrochemical process, slows the penetration of corrosive media, effectively blocks the bottom plate corrosion, and thus improves the corrosion resistance.



Figure 6. Polarization curves of different samples

3.4.2 Electrochemical impedance analysis

The open circuit potentials of the substrate and the polyurethane resin coating are -1.0342 V and -1.03387 V, respectively; the electrochemical impedance spectrogram is shown in figure 7. From figure 7(a), the semicircular (capacitive arc) appears in the IF region of the substrate, indicating that the electrode reaction is a charge transfer process, and the reversely flattened arc in the low frequency region is the contribution of the electrode surface adsorption process. The polyurethane resin coating with an IP-GO content of 0.3% by weight has a larger capacitance-resistance arc than the substrate, and the corrosion resistance is greatly enhanced. That is, the coating blocks the entire electrochemical reaction and greatly improves the corrosion resistance of the galvanized sheet. From

the figure (b), the coating's impedance is nearly 1.5 orders of magnitude larger than the substrate, which is consistent with the Nyquist plot.



Figure 7. EIS spectra of different samples in 3.5% NaCl solution of (a) Electrochemical impedance spectra of substrate and 0.3wt% IP-GO, (b) Bode Phase angle diagrams of coatings.

4. Conclusion

In this experiment, the modified graphene oxide and polyurethane resin are grafted and the modified polyurethane resin is successfully prepared. The corrosion resistance of the polyurethane coating to the galvanized sheet is improved. The polyurethane used is environmentally friendly water-free polyurethane. In addition, the influence of the addition of modified graphene oxide on the corrosion resistance of polyurethane has been studied. It can be concluded that when the IP-GO content is 0.3 wt%, the polyurethane coating has the best corrosion resistance.

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