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Study on the Properties of Silicon-Modified Polyurethane Anticorrosion Coating

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Polyurethane anticorrosion coating has been widely used as a metal coating material in recent years, but it has some shortcomings in hydrophobicity, heat resistance and hardness. In this paper, we add organic silicon to improve the performance of polyurethane through chemical modification. We show that the addition of organic silicon improves the chemical stability of polyurethane based on chemical rules, and prepare polyurethane prepolymer and add organic silicon to test its performance in the form of experimental study. The experimental results show that the addition of organic silicon can improve the contact angle, hardness and impact strength of polyurethane coating. This study is of theoretical guiding significance to the performance improvement of polyurethane and its application in the anticorrosion coating.

1. Introduction

Among various types of anticorrision coatings, polyurethane coating (Melchiors et al., 2000; Rusman et al., 2017; Gabriel et al., 2016) has been widely used as finish in the heavy-duty anticorrosion system due to its excellent wear resistance, low temperature resistance, chemical resistance, flexibility, good adhesion to substrate, excellent physical and mechanical properties and corrosion resistance (Mathew and Singho, 2015). At the same time, polyurethane is also a new organic polymer material, known as the “fifth largest plastic”. Due its excellent performance, it has been extensively studied by countries all over the world. It is reported that the proportion of polyurethane in the coating field represents the coating industry level of a country (Yang et al., 2009). However, the drawbacks of pure polyurethane coating in hydrophobicity, heat resistance and hardness have limited its application in practice. Therefore, polyurethane is usually modified to achieve better performance (Li et al., 2009). Organic silicon resin is excellent in terms of hydrophobicity, resistance to high and low temperature, weather resistance and physiological inertia, etc. We use organic silicon to modify the polyurethane resin into silicon-modified polyurethane resin with good overall performance (Jena et al., 2007; Yekeen et al., 2017). In this paper, we prepare polyurethane prepolymer, and add appropriate dose of organic silicon and other chemical reagents to configure it into silicon-modified polyurethane prepolymer coating. We adopt an appropriate testing method to test the hydrophobicity and hardness of the silicon-modified polyurethane coating with different amounts of organic silicon added -4%, 6%, 8% and 10% and analyze the test results. The results show that the addition of organic silicon can well improve the hydrophobicity, hardness and impact strength of the coating.

2. Test preparation

2.1 Testing materials, equipment and methods

2.1.1 Main testing materials and equipment

The main testing materials for the preparation of polyurethane prepolymer include toluene diisocyanate, polyether diol, dibutyltin dilaurate, dimethyl silicone oil, diethylene glycol, trimethylolpropane, Foamex810, natural graphite (325 mesh), potassium persulfate, phosphorus pentoxide, sulfuric acid, potassium permanganate, hydrogen peroxide, hydrochloric acid, acetone, sodium chloride (Popoola et al., 2016).

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The main testing equipment include electronic balance (CP214), digital thermostat water bath (HH-4), lab spray dryer (YC-015), oil-free air compressor (OTS-750), programmable salt spray test chamber MY-KCY-60A) and electrochemical workstation (CH1760E).

2.1.2 Material characterization test method

(1) Contact angle test (Dong and Li, 2016) is to test the wettablity of the liquid on the solid surface or the waterproofness of the solid. We let the coating sit for 7 days, keep the surface of the coating dry, clean and smooth, collect the images and read the contact angle α between the coating-air (1-g) interface and the glass slide-water drop (s-1) interface. The more hydrophobic the coating is, the greater the contact angle will be. If the coating is hydrophilic, water drops will be distributed evenly on the coating with $\alpha = 0°$.

(2) Hardness test is the basic standard for coating characterization. According to the testing method provided in GB/T 6739-1996 *Determination of Film Hardness by Pencil Test*, we scrape the coating for five times. If there are fewer than 2 scratches on the coating, the pencil hardness is equivalent to the coating hardness (Maria et al., 2001).

(3) Impact strength test is to test whether the coating will peel off the substrate under external high-speed load. We carry out the test by reference to GB/T1732-1993 *Determination of Impact Resistance of Film*. We first place the sample plate on the test bench (Liuzzi and Stefanizzi, 2016), and then strike the sample plate with a hammer of fixed mass. The maximum height (cm) from which the hammer falls on the sample plate and does not damage the film is regarded as the impact strength of the film. There are also some requirements for the impact location – usually it should be at least 15mm from the edge of the sample plate, and the selected location in each test should be at least 15mm away from the surrounding test points (Prabu and Alagar, 2004). Usually, we drop a 1Kg weight from a certain height (Xcm) to impact the pounding head, which then impacts the coating surface, and then we observe it with a 4-time magnifying glass to see whether there are any cracks, wrinkles and peeling on the coating. If there is no such problem with the coating, it indicates that the impact strength of the coating is XKg·cm. One sample plate should be subjected to three impact tests (Galhenage et al., 2016).

2.2 Preparation of polyurethane prepolymer coating

The preparation process of polyurethane prepolymer coating is shown in Figure 1. In this paper, in the chemical modification test, the ratio between –NCO and –OH is 2:1.

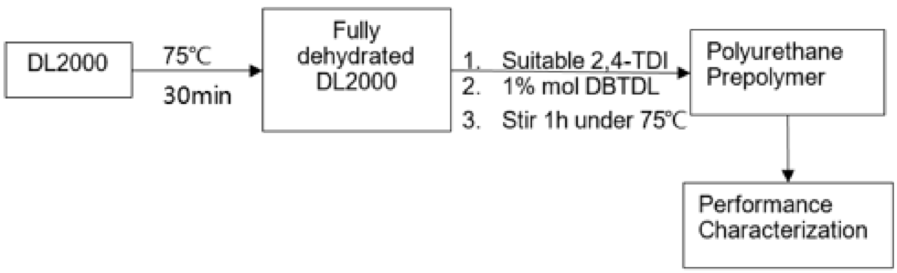

Figure 1: Flow chart for polyurethane prepolymer preparation

2.3 Preparation of silicon-modified polyurethane prepolymer coating

2.3.1 Principle analysis on polyurethane chemical modification

The chemical main chain of the organic silicon is Si-O-Si. As its organic group is directly connected with the silicon atoms, it has the properties of both inorganic and organic materials - it can effectively reduce the surface tension and highly compressible. The combination of organic silicon and polyurethane can improve the tensile capacity and elastic recovery (Guo et al., 2009). The chemical modification method is to utilize the –OH on the organic silicon end to react with the -NCO group on the polyurethane prepolymer chain end so as to introduce the organic silicon into the polyurethane chain and produce the Si-O-C bond block (Bao et al., 2014). The principle for this reaction is shown in Formula 1:

$$\text{-N=C=O+HO-} \rightarrow \text{-NH-COO-} \quad (1)$$

2.3.2 Preparation process of silicon-modified polyurethane prepolymer coating

We adopt the mechanical feeding method. We first place the polyurethane prepolymer in a beaker, weigh the right amount of modifier (dimethyl silicone oil), chain extender (diethylene glycol), cross-linking agent (trimethyl propanol) and foaming agent (Foamex 810), add them into the beaker in order, control the reaction time and

temperature, and keep stirring. In the cooling process, we remove the modified coating. After being placed in water bath at 75 °C and painted and molded, it undergoes the performance test (Biserni and Garai, 2016).
The performance test is carried out on the polyurethane added with different amounts of organic silicon (Król et al., 2015). The composition of the silicon-modified polyurethane composite coating with an organic silicon mass percent of 4%, 6%, 8% and 10% is listed in Table 1 (Liu et al., 2010):

Table 1: Composition of silicone modified polyurethane composite coatings

Code	PDMS-4%	PDMS-6%	PDMS-8%	PDMS-10%
TDI	3.5g	3.5g	3.5g	3.5g
DL2000	20g	20g	20g	20g
DIBUTYLTIN DILAURATE	0.1g	0.1g	0.1g	0.1g
SIMETHICONE	0.6g	0.9g	1.2g	1.5g
DIGLYCOL	0.3g	0.3g	0.3g	0.3g
TRIMETHYLOLPROPANE	0.2g	0.2g	0.2g	0.2g
DEFOAMER	0.1g	0.1g	0.1g	0.1g

3. Test on characteristic properties

3.1 Test and analysis on the contact angle of the silicon-modified polyurethane coating

Chapter 2 It can be seen from the figure that with the addition of organic silicon, the contact angle between polyurethane coating and water increases rapidly from 71°C. When the amount of organic silicon added is 6%, the contact angle reaches the maximum and then decreases with the increase of the amount added. As the organic silicon reacts with polyurethane, forming graft copolymer, the chemically modified material has greater molecular weight and is more hydrophobic. When the amount of organic silicon added reaches a certain value, the dimethyl silicone oil is too much to be bonded with polyurethane, and thus the water solubility is large, leading to smaller contact angle.

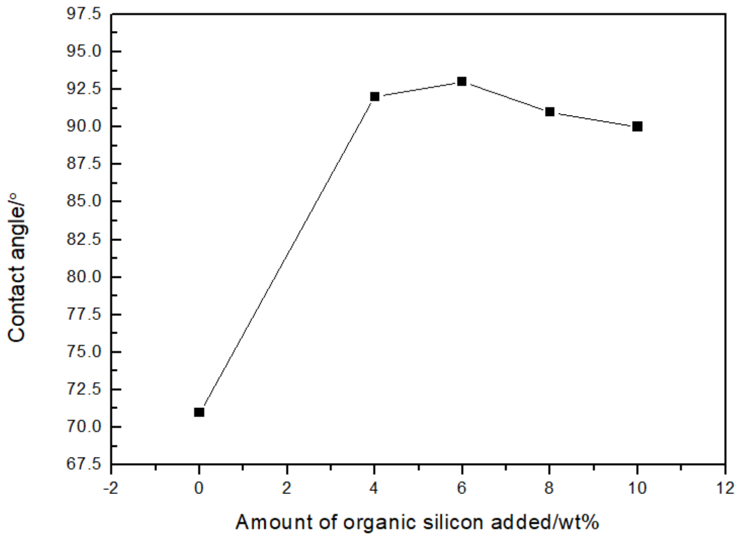

Figure 2: Effect of Silicone Addition on Contact Angle of Composite Coating

3.2 Test and analysis on the contact angle of the silicon-modified polyurethane coating

According to the pencil test method mentioned in the previous section, we test the hardness of the chemically modified polyurethane coating. As can be seen from Figure 3, when the amount of organic silicon added is 6%, the hardness of the coating is the highest. The reason is the same with the contact angle test – when the amount of organic silicon added reaches a certain value, the graft is saturated and additional amount will have a negative impact on the hardness.

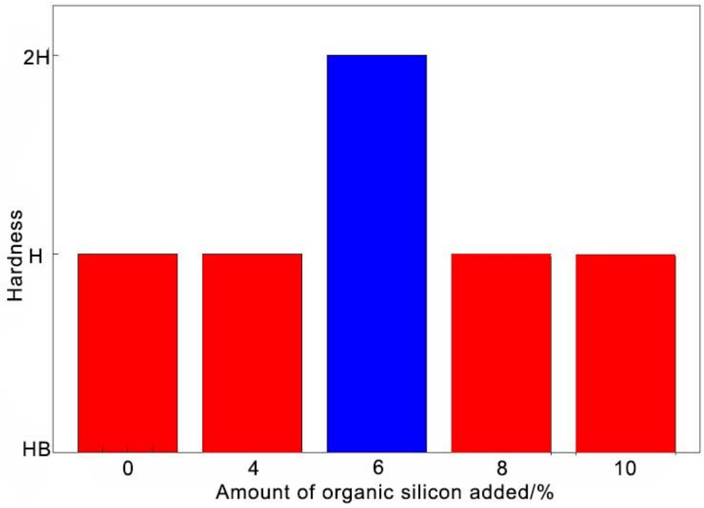

Figure 3: Effect of Silicone Addition on Hardness of Composite Coating

3.3 Impact strength test on the silicon-modified polyurethane coating

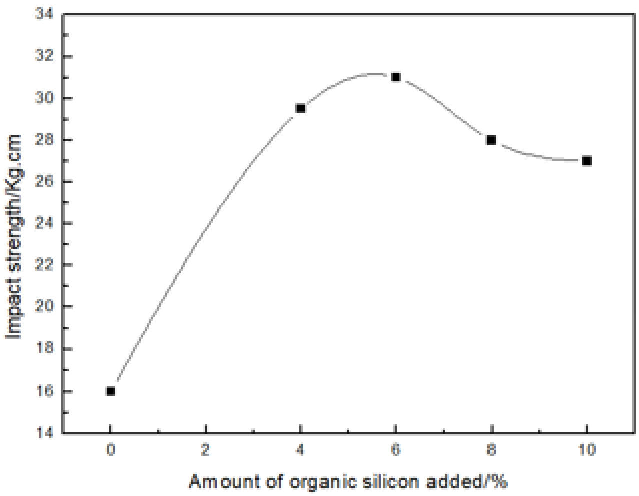

Figure 4: Effect of Silicone Addition on Impact Strength of Composite Coating

It can be seen from the figure that when the organic silicon is 6%, the impact strength is the greatest. Overall, when the amount of organic silicon added is between 4%-10% the impact strength of the polyurethane coating is significantly increased. With the addition of organic silicon, in the molecule, the -OH group reacts with the -NCO group, forming a chemical polymer with a larger molecular weight, so that the impact strength of the composite coating is improved. With the further addition of organic silicon, the small molecules of organic silicon mixed in the polymer will reduce the impact strength.

4. Conclusions

In this paper, we prepare polyurethane prepolymer and add organic silicon into it to test the contact angle, strength and impact strength of the chemically modified material. The conclusions are as follows:

(1) The addition of organic silicon can greatly improve the contact angle, strength and impact strength of polyurethane coating. When the amount of organic silicon added is 6%, the contact angle of the chemical modification coating is increased from 72° to 93°, the hardness is twice the original value, and the impact strength is increased from 16Kg.cm to 32Kg.cm.

(2) The grafting of the -OH molecular chain of organic silicon and the -NCO molecular chain of polyurethane coating improves the properties of chemical modification coating, making it more applicable in engineering anticorrosion.

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