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Synthesis of DC–3074 and Z–1 Silicones Modified Epoxy Resin and Comparison of Salt Spray Resistance

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In order to improve the chemical resistance of epoxy resin and its toughness and corrosion resistance, in this paper, silicone modified epoxy resin was prepared with epoxy resin and two kinds of silicones, Dow Corning DC–3074 and Chenguang Z–1, as raw materials and dibutyltin dilaurate (DBTDL) as catalyst. The structure of the modified epoxy resin was characterized by Fourier transform infrared (FTIR) spectrometer and its performance was tested. The results showed that the epoxy resin modified by DC–3074 had better salt spray resistance compared with the Z–1. Therefore, the DC–3074 was selected as the epoxy resin E–51 modifier. The silicone modified resin was further synthesized with E–51 as the matrix resin, 12.5% DC–3074 silicone as the modifier, and 0.5% DBTDL as the catalyst. The obtained cured coatings showed good performance with the following results: product fineness of 20–25 μm, solid content of more than 95%, surface drying time of 25 min, smooth appearance, hardness of 2 H, adhesion level of 0, and salt spray resistance time of 432 h. The prepared modified epoxy resin coating has good salt spray resistance and good application prospect.

Keywords: Hardness, Modification, Salt spray resistance, Silicone

Introduction

Metal materials are damaged by the action of surrounding medium, and corrosion problems are widespread. Metal corrosion not only brings great economic losses to the national economy, but also causes environmental pollution. Preparation of anti-corrosion coating is one of the most effective methods to slow down the corrosion rate.[1,2] Epoxy resin is a kind of thermosetting polymer with more than two epoxy groups. When it reacts with curing agent, which can form a three-dimensional network structure, and basically does not produce small molecular volatiles.[3] The secondary hydroxyl and epoxy groups in the molecule give the resin reactivity, which makes it have strong cohesive force and good adhesion to the substrate.[4] Ether bonds and hydroxyl groups are polar groups that help improve wettability and adhesion.[5] Epoxy resin has good adhesive strength, corrosion resistance, electrical insulation, high strength[6,7], and it is widely used in the field of anti-corrosion coatings to prevent corrosion of metal materials.[8] Resin anticorrosive coatings cross-linked through epoxy groups to form a film with high adhesion and corrosion resistance. The coating has low relative cost and meets the development requirements of low pollution, which is a hot spot in the development of modern coatings.[9]

However, the content of benzene ring in epoxy resin is large, which leads to rigidity, limited molecular chain movement and low flexibility.[10] Curing cross-linking structure is not easy to deform, resulting in poor toughness, brittleness, low peel strength.[11–12] In addition, due to the small energy of C–C bond in epoxy resin, it is easy to decompose and yellow at high temperature, which determines the poor heat resistance and limits the use of anticorrosive coatings in high temperature environment.[13] Therefore, the unmodified epoxy resin is difficult to meet the increasingly stringent requirements of engineering technology, which limits its wide application and reduces the competitiveness.[14] It is essential to modify epoxy resin to improve its toughness and corrosion resistance. At present, epoxy resin modified by organic silicon is a hot research topic. The main reason is the existence of –Si–O–Si– in organosilicon. The Si–O bond energy can reach 460 kJ/mol, which is greater than the C–C bond energy of 345 kJ/mol. This makes the organic silicon products have relatively high thermal stability.[15,16] In

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addition, silicone not only has the characteristics of flexibility and formability, but also has the advantages of non-toxicity and chemical resistance.[17] Epoxy resin modified by silicone can improve the thermal stability, weather resistance and toughness. Many scholars have done a lot of work in this regard.[18,19]

Therefore, in order to improve the chemical resistance, toughness and corrosion resistance of epoxy resin, the silicone modified epoxy resin was prepared by using DC-3074 and Z-1 silicone with an appropriate amount of phenyl in this paper. The organic siloxane as the modifier had excellent thermal and oxidation stability, and can enhanced the hydrophobicity of E–51. In addition, the compatibility between silicone and epoxy resin was further improved by the presence of appropriate amount of phenyl. The mechanical properties and salt spray resistance of modified resin were significantly improved.

Materials and methods

Material and Instruments

Epoxy resin (E–51) was supplied by Henan Jinfeng Chemical Co., Ltd. China. DC–3074 was purchased from Dow Corning Company, USA. Z–1 was purchased from Jiangsu Chenguang Coatings Co., Ltd. China. Dibutyltin dilaurate was purchased from chemical reagent company of China Pharmaceutical Group. Polyetheramine D–230 was purchased from Hensman Company, USA. Concentrated hydrochloric acid, potassium hydroxide, acetone, sodium chloride (NaCl)were purchased from Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. China.

The following techniques were used in the experiment: Electronic balance (JY502, Shanghai Shunyu Hengping Instrument Factory). The collector constant temperature heating magnetic stirrer (DF–101S, Gongyi Yuhua Instrument Co., Ltd.). Electric mixer (DW–1, Jintan Zhongda Instrument Factory). Circulating water multi-purpose vacuum pump (SHZ–D (III), Henan Yuhua Instrument Co., Ltd.). Electric hot blast dryer (FBX101–3, Shanghai Jianqi Instrument Co., Ltd.). Fourier transform infrared spectrometer (Nicolet iS5, American Semerfeld Technology Co., Ltd.). Wire rod coating (Aichi Hardware Store). Scraper Detail Meter (Aichi Hardware Store). Coating adhesion tester (Aichi hardware store); pencil hardness meter (Aichi hardware store).

Preparation of Silicone Modified Epoxy Resin

Epoxy resin and silicone were added into four flasks with mechanical stirrer in different proportions, and a certain amount of deionized water was added. Dibutyltin dilaurate (DBTDL, epoxy resin mass 0.5%) was used as catalyst. Nitrogen was introduced into the four flasks to replace the air for three times, and then the heating and stirring were started. The reaction was carried out in nitrogen atmosphere and at 100–130°C for 2–5 h. After the reaction was over, the nitrogen was stopped after the temperature dropped to room temperature. The catalyst was extracted for 3–5 times with deionized water at 80°C, and the samples were collected after vacuum distillation. The experimental scheme is shown in Fig. 1.

Product performance test

The epoxy value of epoxy resin was measured according to the national standard[20] GB/T 1677–2008, using the hydrochloric acid acetone method.

The performance of the cured coating was tested after drying at room temperature for one week.

Curing Reaction of Epoxy Resin

The curing reaction of epoxy resin was shown in Fig. 2. Polyether amine D–230 was used as the curing agent. Firstly, the active hydrogen on primary amine reacted with one molecule of epoxy resin to produce secondary amine, and then further reacted with another molecule to produce tertiary amine. Finally, a cross-linked network structure was formed.

The amount of curing agent was calculated using the following equation (Eq.1),

$$m(\text{curing agent}) = m(\text{resin})E/N(H) \qquad \ldots (1)$$

where, E is epoxy value; N(H) is the number of active hydrogen atoms of curing agent. The theoretical mass

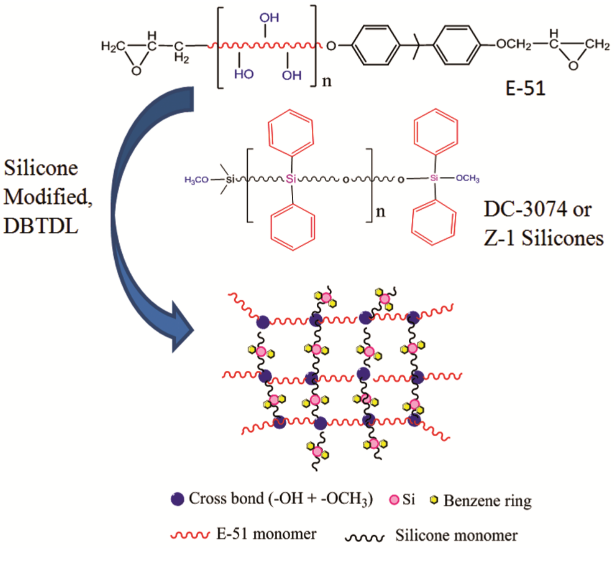

Fig. 1 — Scheme for silicone modified epoxy resin

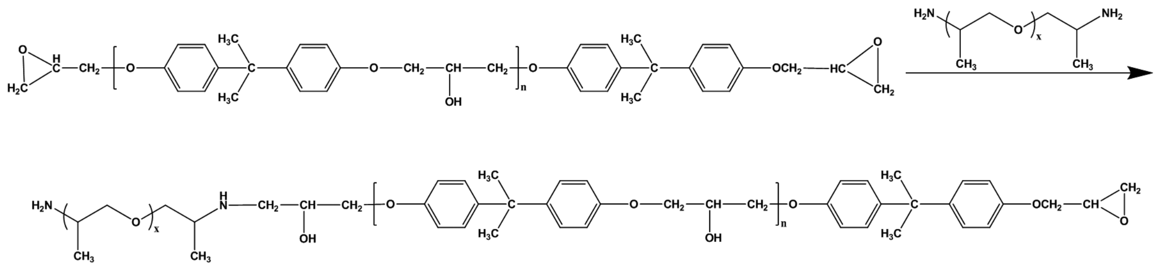

Fig. 2 — Curing reaction of epoxy resin

of the curing agent was calculated by Eq. (1). E–51 and D–230 were mixed uniformly at room temperature and applied to the pre-treated tinplate sheet. Then, it was put into the electric heating blast drying oven and heated at 80°C for 30min to obtain the cured products. The coating was dried at room temperature for one week and then the properties of the coating were tested.

Infrared characterization of silicone modified epoxy resin

The purified samples were scanned by the FT–IR200 Fourier Transform Infrared spectrometer.

Results and Discussion

Reaction Mechanism of Silicone Modified Epoxy Resin

The reaction mechanism of E–51 modified DC–3074 silicone was shown in Fig. 3. The active terminal groups of silicon, such as alkoxy, hydroxyl and amino, reacted with hydroxyl or epoxy groups in epoxy resin to form stable Si–O–C bonds and form block polymers. Polysiloxane segment had strong non-polarity, hydrophobicity and low surface free energy.[21] Because the flexibility and heat resistance of the silicone reduce the internal stress, the toughness and chemical resistance of the epoxy resin are improved. The modified epoxy resin coating had stronger water barrier and adhesion to metal matrix. This may be due to the increase of the concentration of unreacted methoxy group, resulting in the increase of its hydrolysis rate and the decrease of water content. In this experiment, silicone was mainly grafted into E–51 molecules through the reaction between alkoxy and hydroxyl groups.[22] The reaction mechanism was that the alkoxy group was hydrolyzed first, and the hydroxyl group reacted with the secondary hydroxyl group of E–51 through dehydration condensation. In the whole process, the epoxy group did not participate in the reaction, which did not reduce the curing crosslink density of the system, but also improved the salt spray resistance of the cured product.

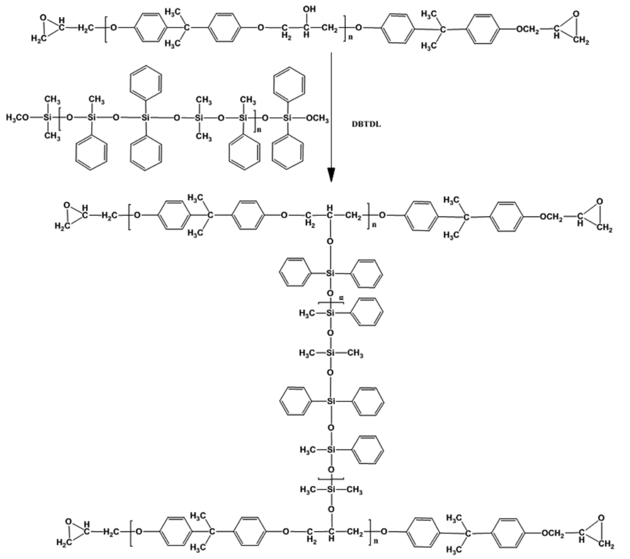

Fig. 3 — The reaction mechanism of DC–3074 Silicone modified epoxy resin

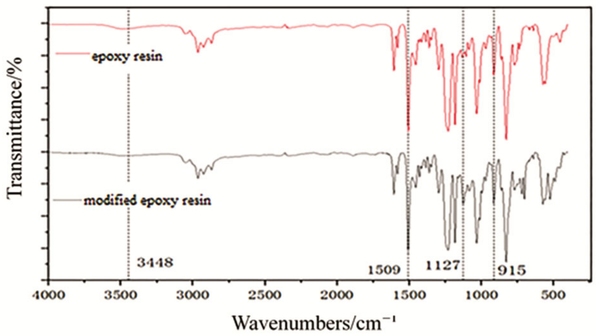

Fig. 4 — FTIR of silicone modified epoxy resin

Infrared Spectroscopy Analysis of Silicone Modified Epoxy Resin

In order to observe and compare the chemical structure of the samples, pure epoxy resin and modified epoxy resin were analyzed by FT–IR spectroscopy and the results were shown in Fig. 4.

It can be seen from Fig. 4 that the absorption peaks of the epoxy group corresponded to 915 cm^{-1} and 1247 cm^{-1}. After the modification, two absorption peaks were basically unchanged, indicating that there is not consumption of epoxy groups in the reaction. The hydroxyl vibration absorption peak of E–51 was at 3500 cm^{-1}, after modification, part of the hydroxyl reacted with silicone, and the hydroxyl absorption peak at 3448 cm^{-1} was significantly weakened. In addition, there was an obvious Si–O bond absorption peak near the 1127 cm^{-1}, indicating that silicone was successfully grafted onto the epoxy resin molecule.

Effect of Silicone Type on Coating Properties

In the experiment, two different silicones were used, with the 10% addition amount of E–51, and reacted at 120°C for 3 hours to explore the effect of silicone on coating properties. See the Table1 for details. The salt spray resistance performance was shown in Fig. 5.

It can be seen from Table 1 that the two silicones, DC–3074 and Z–1, only reacted with the hydroxyl group of epoxy resin in the reaction process, and did not react with the epoxy group. Therefore, the epoxy values were 0.458 and 0.460, respectively, the difference between the two values was small, and the crosslinking density of the cured resin will not be reduced. Compared with Z–1, the salt spray resistance time of DC–3074 modified coating was increased by 48 h. Although the two kinds of silicone only consumed the secondary hydroxyl of the epoxy resin during the reaction, the phenylmethyl ratio of DC–3074 was close to 1:1, and its salt spray resistance time was longer than that of Z–1.

Fig. 5 — Comparison of salt spray resistance of different silicone modified epoxy resins: (a) DC–3074 modified epoxy resin, (b) Z–1 modified epoxy resin

It can be seen from Fig. 5 that salt spray resistance of epoxy resin modified by DC–3074 was better, the cured coating was smooth without bubbles, cracks and flaking, which was consistent with the result of long salt spray resistance time in Table 1. Therefore, the silicone DC–3074 was selected as the silicone modifier.

Effect of Silicone Addition on Coating Properties

The DC–3074 was used as epoxy resin modifier and reacted at 120°C for 3 h to explore the effect of silicone addition on the performance of the coating. The results were shown in Table 2. The changes of the salt spray resistance time were shown in Fig. 6.

It can be seen from Table 2 that with the increase of silicone content, the performance of modified epoxy resins and its cured products was gradually getting better. From Fig. 6, it can be seen that the salt spray resistance time of the coating increased from 360 h to 432 h. when the silicone content reached 15% of the epoxy resin mass, the salt spray resistance time began

Table 1 — Effect of silicone types on properties of coatings

Types of Silicone	DC–3074	Z–1
Epoxy value	0.458	0.460
Fineness (μm)	20	20
Viscosity (mPa·s)	—	—
Non-volatile content (%)	98.2%	97.9%
Curing time (min)	30	30
Coating appearance	even	even
Adhesion	0	0
Hardness	2 H	2 H
Salt spray resistance time (h)	384	336

Table 2 — Effect of silicone addition on properties of modified epoxy resin coatings

m(DC–3074)/m(EP)(%)	8	10	12	15	18
Epoxy value	0.469	0.461	0.452	0.437	0.431
Fineness(μm)	20	20	20	20	20
Viscosity(mPa·s)	—	—	—	—	—
Non-volatile content(%)	98.3	98.7	97.5	97.3	98.9
Coating appearance	even	even	even	even	even
Adhesion	0	0	0	1	1
Hardness	2 H	2 H	2 H	3 H	3 H

to decrease. When the amount of silicone added was too large, a part of silicone cannot be grafted into the epoxy resin molecule, and can only be mixed in the liquid, resulting in the existence of a part of free silicone. In the curing stage, free silicone was embedded in the network structure, which was connected with the epoxy resin by hydrogen bonding. Since the hydrogen bond energy was relatively weak compared with the chemical bond, it was easy to break under the action of external force (such as heating, ion attack, etc.), which affected the compactness of the coating, led to the decrease of salt spray resistance. Therefore, the appropriate amount of silicone DC–3074 was 12% of the amount of epoxy resin.

Effect of Reaction Temperature on Coating Properties

The 12% (based on the amount of epoxy resin, wt.%) silicone DC–3074 was used as epoxy resin modifier and reacted for 3h to explore the effect of reaction temperature on the performance of coatings. The results were shown in Table 3. The changes of the salt spray resistance time of the coating were shown in Fig. 7.

It can be seen from Table 3 that when the reaction temperature was less than 120°C, the epoxy values was almost unchanged. The alkoxy group reacted with the secondary hydroxyl group without consuming the epoxy group, which can improve the crosslink density of the cured product. At 130°C, the epoxy value began to decrease, indicating that the epoxy group was opened the ring at high temperature, which affected the crosslinking of the cured product. As can be seen from Fig. 7, the salt spray resistance time of the product cured at 110°C was shorter than that of at 120°C, indicating that the organic silicon cannot be fully integrated into the epoxy resin at 110°C, so 120°C was considered to be the appropriate reaction temperature.

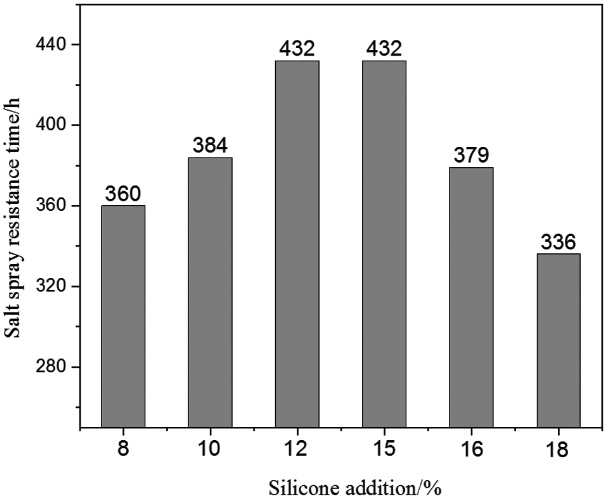

Fig. 6 — Effect of silicone addition on the salt spray resistance time of coatings

Effect of Reaction Time on Coating Properties

The 12% (wt.%) silicone DC–3074 was used as the epoxy resin modifier to react at 120°C to explore the effect of reaction time on the performance of coatings. The results were shown in Table 4.

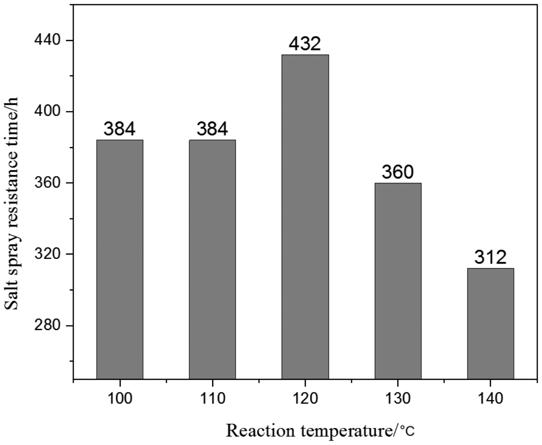

Fig. 7 — Effect of reaction temperature on the salt spray resistance time of coatings

Table 4 — Effect of reaction time on properties of modified epoxy resin coatings

Reaction time (h)	2	3	4	5
Epoxy value	0.447	0.452	0.449	0.453
Fineness(μm)	30	20	20	20
Viscosity (mPa·s)	—	—	—	—
Non-volatile content (%)	96.7	96.2	97.4	97.9
Curing time (min)	30	30	30	30
Adhesion	0	0	0	0
Hardness	2 H	2 H	2 H	2 H
Salt spray resistance time (h)	360	432	408	336

Table 3 — Effect of reaction temperature on properties of modified epoxy resin coatings

Reaction temperature (°C)	100	110	120	130	140
Epoxy value	0.455	0.449	0.451	0.431	0.417
Fineness (μm)	20	20	20	20	20
Viscosity (mPa·s)	—	—	—	—	—
Non-volatile content (%)	98	96.9	97.4	97.8	96.7
Adhesion	0	0	0	0	0
Hardness	2 H	2 H	2 H	2 H	2 H

It can be seen from Table 4 that when the reaction time was less than 3 h, the product fineness was large and the salt spray resistance was not good. The reason is that when the reaction time was short, some organic silicon did not react with the hydroxyl of epoxy resin, and it was mixed with liquid but cannot dissolve. The compatibility between silicone and epoxy resin was poor. Moreover, the particle size of the residual silicone was large, which increased the fineness of the epoxy resin. When the epoxy resin was cured, the large particle in the coating led to more voids, which reduced the chemical resistance of the modified epoxy resin. When the reaction time was more than 2 h, with the increase of reaction time, the product fineness decreased and the salt spray resistance time increased. After 3 h, the fineness was almost unchanged, indicating that the organic silicon is almost completely reacted. When the reaction time reached 4 h, the epoxy value decreased, indicating that the epoxy group was opened the ring, which will lead to the decrease of crosslink density and salt spray resistance time. Therefore, choose 3 h as the appropriate reaction time.

Conclusions

Organic silicone modified epoxy resin was prepared, when the addition amount of silicone was 12% (wt.%), the reaction temperature was 120℃ and the reaction time was 3 h, the solid content of the prepared coating was above 95%, the drying time was 30 min at 80℃, and the appearance of the coating was smooth, no cracking, blistering and peeling. After curing at room temperature for seven days, the hardness of the coating reached 2 H, the adhesion was 0 grade, and the salt spray resistance time can reach 432 h. Compared with pure epoxy resin, the hardness, adhesion and salt spray resistance of silicone modified epoxy resin cured coatings are greatly improved. It has a good application prospect in the field of metal anti-corrosion coatings.

Conflict of interest

All authors declare no conflict of interest.

Acknowledgement

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