

Synthesis of Diphenyl Silanediol Modified Epoxy Resin and Its Salt Spray Resistance

Hua Li^{1,2,*}, Zhonghua Yang², Hanhan Yang²

¹Henan Provincial Engineering Laboratory of Coal-based Ecological Fine Chemicals, Jiyuan, 459000, China

²School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, China

*corresponding author.

Keywords: epoxy resin, silicone, modification, salt tolerance resistance

Abstract: In this research, modified epoxy resin was synthesized by using epoxy resin and Dihydroxydiphenylsilane (DHDPS) as raw materials and stannic caprylate (SnOct) as catalyst. The structure of the modified epoxy resin was characterized by fourier transform infrared (FTIR) spectrometer. Results showed that the modified epoxy resin had a hardness of 2H, adhesion of 0 class and good salt spray resistance under the condition of mass ratio of E-51:DHDPS, reaction temperature of 120°C and reaction time of 3 h. At the same time, effect of catalyst on the reaction of modified epoxy resin was studied, results showed that the structure of modified epoxy resin with SnOct as catalyst is similar to that of dibutyltin dilaurate (DBTDL), but SnOct is relatively environment-friendly, with strong catalytic activity and lower cost than that of DBTDL.

1. Introduction

Epoxy resin is highly cross-linked thermoset polymers with good chemical resistance, good bonding, good electrical insulation and high strength. The polymer has been widely utilized in industrial, such as electronic circuit board laminates, electronic packing, adhesives and corrosion resistant coating systems [1-4]. However, the disadvantages of epoxy resin with a three-dimensional network structure, lacking of sliding between the molecular chains, low energy between C-C and C-O bond, high surface energy and hydroxyl groups existence, etc. strict their salt spray resistance of coatings. Therefore, the development of modified epoxy resin with good salt resistance is necessary.

At present, there are numerous approaches to improve the performance of the epoxy resin, in which, the method of introducing silicone resin into the epoxy resin network have drawn much attention and turned out to be an effective way, because the Si-O bond energy of the silicone resin is far higher than that of the C-C [5-9].

However, most of the silicone resin modified epoxy resin need consume the epoxy group, but if the epoxy group were consumed in advance, it can greatly reduces the cross-linking of curing process and the salt spray resistance of coatings. At the same time, the large amounts of methyl group reduced the compatibility of epoxy resin with silicone, that inevitably resulted in a poor salt spray resistance and mechanical properties of the modified resin. Besides, DBTDL, the catalyst, was mainly used in silicone-modified epoxy resin, which is not only highly toxic, but also high in cost. To solve the problem, a kind of silicone resin modified epoxy resin were prepared by the DHDPS and epoxy resin. The phenyl improved the compatibility between silicone and epoxy resin and Si-O-C bond enhanced the salt spray resistance of resin. At the same time, owing to the toxic DBTDL catalyst was replaced by SnOct, it can reduce the cost and make the process more environment-friendly.

2. Experimental part

2.1 Material and instruments

Material:

Epoxy resin (E-51) was supplied by Henan Jinfeng Chemical Co., Ltd. China. Dihydroxydiphenylsilane(DHDPS) was purchased from Sinopharm Chemical Reagent Co., Ltd. China. Stannic caprylate(SnOct) was purchased from Sinopharm Chemical Reagent Co., Ltd. China. Silane coupling agent KH-560 was purchased from Shandong Yousuo Chemical Technology Co., Ltd. China. Polyetheramine D-230 was purchased Nanjing Yuzhuo Material Technology Co., Ltd. China. Hydrochloric acid was purchased from Tianjin Sailboat Chemical Reagent Technology Co., Ltd. China. Potassium hydroxide was purchased from Tianjin Sailboat Chemical Reagent Technology Co., Ltd. China. Acetone was purchased from Tianjin Sailboat Chemical Reagent Technology Co., Ltd. China. Methyl red was purchased from Tianjin Sailboat Chemical Reagent Technology Co., Ltd. China. Sodium chloride (NaCl) was purchased from Tianjin Sailboat Chemical Reagent Technology Co., Ltd. China. All of the materials utilized in this study were used directly without further purification.

Apparatus:

Electronic balance (JY502, Shanghai Hengping Instrument and Meter Factory); collector type constant temperature heating magnetic stirrer (DF-101S, Henan Boze 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 blast drying oven (FBX101-3, Shanghai Shuli Instrument Co., Ltd.); Fourier infrared spectrometer (Nicolet iS5, American Thermo Fisher Technology Co., Ltd., wire bar applicator (Aice hardware franchise store); scraper fineness meter (Aice hardware franchise store); paint film adhesion tester (Aice hardware franchise store); pencil hardness tester (Aice Hardware franchise store)

2.2 Preparation of silicone modified epoxy resin

Epoxy, DHDPS (5, 10, 15 and 20 wt.%) and KH-560 (2 wt.%) were taken in a four-necked flask and SnOct (1 wt.%) was used as catalyst. The above mentioned mixture was heated and maintained at 110~140 °C under an inert nitrogen atmosphere with continuous stirring for 2~4 h to form DHDPS modified epoxy.

2.3 Determination of epoxy value

The epoxy value of the epoxy resin was measured by the hydrochloric acid acetone method shown in GB-T1677-2008.^[10]

2.4 Curing of epoxy resin

The curing reaction of the epoxy resin is shown in Figure 1. The polyetheramine D-230 is used as a curing agent, and it reacts with the active hydrogen from the primary amine of epoxy resin to generate secondary amine. Finally, the crosslinked network structure is formed.

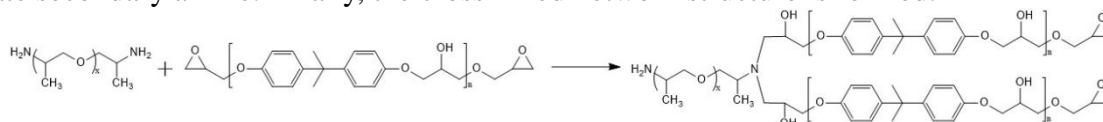


Fig.1 curing reaction of epoxy resin

The amount of curing agent was calculated as follows,:

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

In which, E is the epoxy value of the epoxy resin; $N(H)$ is the number of active hydrogen atoms of the curing agent. The theoretical quality of the curing agent required for curing the epoxy resin can be calculated according to Eq. 1, epoxy resin and DHDPS were mixed at room temperature uniformly, and were applied to the treated tinplate, and were heated in an electric blast drying oven at 80 °C for 30 min^[10]. A modified resin cured product was obtained.

2.5 Characterization of Silicone Modified Epoxy Resin

The infrared spectrum was measured by a Fourier transform infrared spectrometer (Nicolet is 5, Thermo Fisher Scientific, Inc.).

3. Results and discussion

3.1 Reaction principle of silicone modified epoxy resin

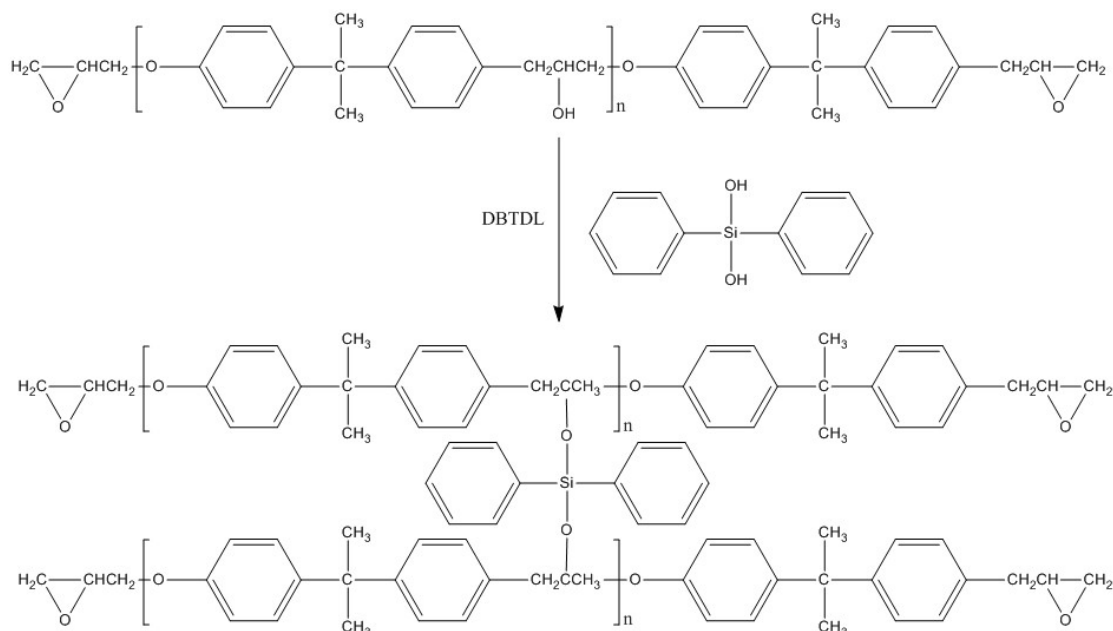


Fig.2 Diphenylsilyl glycol modified epoxy resin

The reaction principle of diphenylsilyl glycol modified epoxy resin is shown in Fig. 2. Since silicone has the advantages of low surface energy, good thermal stability, oxidation resistance and low flexibility, therefore its reactive end groups such as hydroxyl, amino and carboxyl groups of silicones can be reacted with the hydroxyl groups or epoxy groups in epoxy resins, and a stable Si-O-C bond can be created, block copolymers can be produced. while utilizing the flexibility and heat resistance of the Si-O bond, the internal stress of the epoxy resin can be decreased, the toughness of the epoxy resin can be increased and the epoxy resin Heat and chemical resistance can be improved. However, if the epoxy group is pre-consumed in the reaction of the silicone-modified epoxy resin, the curing crosslink density of the system is lowered, which influence the improvement of the salt spray resistance of the modified resin. In this experiment, the reaction of diphenylsilyl diol with the hydroxyl group on the side chain of the epoxy resin not only does not reduce the curing crosslink density of the system, but also improves the salt spray resistance of the cured product.

3.2 FTIR analysis of modify epoxy resin

The following two reactions may occur between diphenylsilanediol and epoxy resin:

① The hydroxyl group of DHDPS reacts with the epoxy group, grafts onto the epoxy resin, and consumes a part of the epoxy group to connect the epoxy resins, but crosslinks the epoxy resin cured product. Reduced density, affecting the salt spray resistance of epoxy resin paint film, see Figure 3;

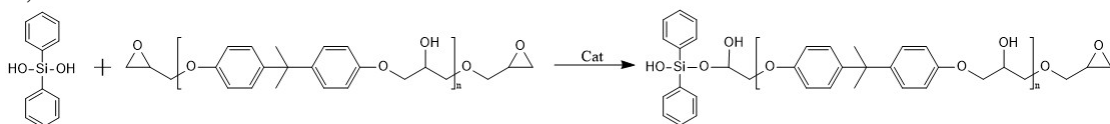


Figure 3 silyl hydroxyl group in the epoxy group reaction

② Diphenylsilane diol reacts with the secondary hydroxyl group of the epoxy resin, and

dehydration condensation of the hydroxyl group causes the diphenylsilane glycol to be grafted onto the epoxy resin. The reaction has no effect on the amount of the epoxy group, and can ensure subsequent The crosslink density of the epoxy resin cured product is substantially unchanged, and the salt spray resistance of the epoxy resin paint film is improved, see Fig. 4;

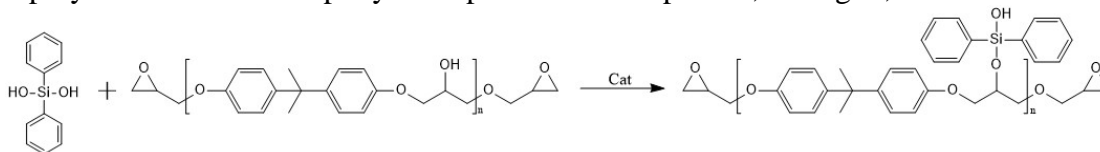


Figure 4 silyl hydroxyl reacts with epoxy side chain hydroxyl groups

The FTIR spectrums of epoxy resin and the modified epoxy resin were shown in Fig. 5.

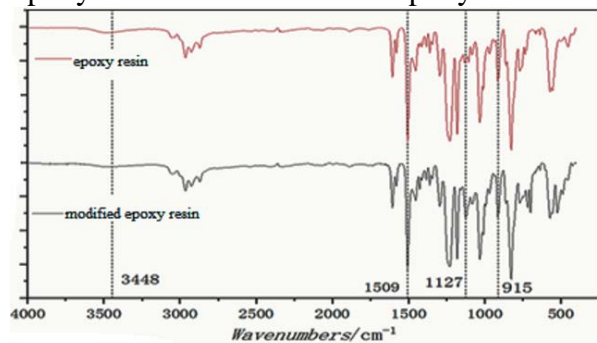


Figure 5: Infrared spectrum of unmodified epoxy resin and modified epoxy resin

In Fig. 5, it shows that the absorption peaks of epoxy groups (915cm^{-1} and 1247cm^{-1})^[11] on the epoxy resin before and after modification are basically unchanged, and the absorption peak of hydroxyl groups (3361cm^{-1}) is significantly reduced, and at 1183.9cm^{-1} at the same time. The absorption peak of Si-O-C bond appeared at $1194, 1089\text{cm}^{-1}$ ^[12-19], indicating that the dehydration condensation reaction of diphenylsilanediol and epoxy resin was carried out on the epoxy resin without substantially depleting the epoxy group.

3.2 Effect of Addition Amount of Silicon on Performance of Modified Epoxy Coating Film

The effect of addition amount of silicone on the properties of the modified epoxy resin coating is shown in Table 1.

Table 1 Effect of the amount of silicone added on the properties of modified epoxy resin coating film

m (DHDPS)/m (EP)%	Adhesion	Hardness	Salt spray resistance time /h
5%	0	2~3H	288
10%	0	3~4H	576
12%	0	3~4H	575
15%	0	3H	384
20%	1	2~3H	216

In Table 1, it shows that when $m(\text{silicone}) / m(\text{epoxy resin}) = 10\%$, salt spray resistance time of the modified epoxy resin is the biggest, with the increase of amount of silicone, the hardness and salt water resistance of the modified epoxy resin is lowered. It is probably that some silicone cannot be grafted into the epoxy resin and can only be mixed in the epoxy resin liquid, and due to the large particle size of the silicone and its polymer, the compatibility with the modified epoxy resin is poor, resulting in more voids in the coating film, lowering the compactness of the coating film.

3.3 Effect of reaction temperature on modified epoxy resin

The epoxy value of the modified epoxy resin at different temperatures was determined by the guanidine hydrochloride-acetone method, and is compared with the theoretical calculation, the results are shown in Table 2. The theoretical epoxy value is calculated by mixing the epoxy resin

raw material with DHDPS without any reaction.

Table 2 Comparison of theoretical epoxy value of silicone modified epoxy resin with measured epoxy value at different reaction temperatures

Transparent/°C	Theoretical epoxy value	Measured epoxy value	Salt spray resistance time /h
100	0.402	0.391	312
110	0.402	0.389	576
120	0.402	0.390	576
130	0.402	0.385	576
140	0.402	0.263	384

In Table 2, it shows that the epoxy value of epoxy resin is almost not changed before and after the reaction except 140 ° C, indicating that the reaction group in the silicone reacts with the secondary hydroxyl group in the epoxy resin at lower than 130 ° C, and can be retained by the epoxy group increases the crosslinking density of the cured product; when the temperature is higher than 130 ° C, the reaction temperature may increase, so that a part of the reactive groups of the silicone react with the epoxy group, and the epoxy group is consumed.

3.4 Effect of reaction time on modified epoxy resin

The effect of reaction time on the modified epoxy resin is shown in Table 3.

Table 3 Appearance and Epoxy Value of Silicone Modified Epoxy Resin under Different Reaction Time

Time/h	Exterior	Theoretical epoxy value	Measured epoxy value	Salt spray resistance time /h
2	24h, turbid	0.402	0.389	408
3	72h, transparent	0.402	0.391	576
4	72h, transparent	0.402	0.390	576
5	72h, transparent	0.402	0.386	576

In Table 3, it shows that when the reaction time is less than 3 h, the modified epoxy resin liquid is turbid, and the salt spray resistance is worse than the other groups. The reason is that when the reaction time is short, some of the silicone does not react with the hydroxyl group of the epoxy resin side chain, they are incompatible, resulting in turbidity of solution, and the particle size of the silicone and the polymer is large thereof. Poor compatibility with the modified epoxy resin results in more voids in the coating film, lowering the compactness of the coating film, and having a greater influence on the chemical resistance of the coating film. When the reaction time is more than 3h, the modified epoxy resin can remain clear for a long time, and the epoxy value is almost not changed, indicating that 3 h is the suitable reaction time.

3.5 Effect of catalyst on the reaction of modified epoxy resin

Table 4 Effect of different catalysts on modified epoxy resin

Catalyst	Dosage/ (g/100gEP)	toxicity	Price/ (yuan/25g)	M	Measured epoxy value	Salt spray resistance time/h
SnOct	0.8	middle toxic	39	405	0.391	576
DBTDL	1	highly toxic	69	631	0.391	576

In Table 4, it is seen that the catalytic effect of SnOct is similar with the catalytic effect of DBTDL, but the price of SnOct is relatively cheap and the molecular mass and toxicity are also

relatively small, so that it is more suitable as the catalyst for the modification of diphenyl silicon glycol.

4 Conclusion

The effects of the ratio of reactants, reaction temperature, reaction time and different catalysts on the modified epoxy resin coatings were investigated. Under the reaction conditions of temperature 120 ° C, m (silicone): m (epoxy resin) = 1:10 and reaction time of 3 h, silicone modified epoxy resin has good salt spray resistance and cured product were prepared.

Compared with the pure epoxy resin coatings, the toughness, adhesion and salt spray resistance of the silicone modified epoxy resin coating film are improved; but with the increase of the amount of silicone, the silicone cannot be completely grafted onto the epoxy resin, and self-polymerization will occur. The residual organosilicon and its polymer remained in the epoxy resin liquid have larger particle size, so the epoxy resin has an increased fineness. After the resin was cured, the larger fineness of coating affects the compactness of the coating film and reduces the chemical resistance of the cured epoxy resin.

FTIR spectroscopy and epoxy value test showed that the epoxy group of the epoxy resin was not involved in the reaction, but the hydroxyl group of the DHDPS was polymerized with the hydroxyl group of the epoxy resin side chain, and the silicone is successfully grafted onto the secondary hydroxyl group of the epoxy resin.

Which low toxicity catalyst of SnOct replaced the toxic DBTDL, can greatly reduce the cost and make the process more environment-friendly.

Acknowledgements

This work was supported by Opening Foundation of Henan Provincial Engineering Laboratory of Coal-based Ecological Fine Chemicals (C202003).

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