



Study on properties of epoxy resin and polyurethane modified with organic silicon

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Abstract: In order to solve the problem of poor compatibility of traditional resins, improve its adhesion, toughness, corrosion, heat resistance, salt spray, and other properties of the coating, the epoxy resin and polyurethane was modified with organic silicon. Some modified methods were introduced and summarized, the prospects for the research development in the future were look forward.

Key words: Epoxy Resin; Organic Silicon; Compatibility; Aminosilicone Oil; Polyurethane; Salt Spray Test

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1. Introduction

Epoxy resin is a polymer oligomer, which contains two or more than two epoxy groups, with aliphatic, alicyclic or aromatic group organic compounds as the skeleton, which can react through the epoxy group to form useful thermosetting products. It has excellent adhesion, excellent electrical insulation, good mechanical properties, good corrosion resistance and chemical resistance are widely used in many fields, such as civil engineering, electrical and electronic engineering, coatings and plastics. However, the heat resistance and resistance to impact damage of epoxy resin are poor. Because of the high elastic wear resistance, brittleness, rub resistance, low temperature resistance, good compatibility and other excellent performances of polyurethane, which is widely used in paint industry. However, polyurethane also has disadvantages, such as poor surface performance, flammability, high temperature resistance and aging. In order to solve the shortcomings of epoxy resin and polyurethane materials, epoxy resin and polyurethane modified with organic silicon were studied. Epoxy resin and polyurethane modified with organic silicon have the effect on complementarity. The modified resin can improve the adhesion, impact resistance, heat resistance and salt spray resistance of the coating. The purpose of this paper is to develop a new type of coating with excellent properties.

2. Methods of epoxy resin and polyurethane modified with organic silicon

2.1 Mechanism and method of epoxy resin modified with organic silicon

At present, the way of organicsilicone modifying epoxy resin mainly includes active terminal group reaction, using silicone coupling agent to form block copolymers, substituting siloxane partial side groups and preparation of polysiloxane particles. According to the reaction mechanism, the method can be divided into two parts: physical blending and graft copolymerization modification.

2.1.1 Physical blending modification

Physical blending is that suitable silicone with epoxy resin, adding curing agent, curing accelerator, additives to form a system with excellent performance. The compatibility of the components in the blends is an important factor affecting the morphology and properties of the blends. Because the solubility parameter of organic silicon (SP) is 7.3-7.5, while that of epoxy resin is 10.09^[1]. The difference is large, so their compatibility is poor. If we simply put them together in the modification, due to interfacial tension, which becomes many phases separation structure, the modification effect is not good. So, people generally increase the transition phase (compatibilizer) or add coupling agent to improve their compatibility.

(1) Introducing in compatibilizer in the molecular structure of organic silicon

By introducing in strongly polar polyether chain groups in the silicone molecules, the polarity of the silicone molecules can be improved, the strong physical interaction between polymer molecules can be obtained, thereby its compatibility with epoxy resin can be increased.

A polyether graft polysiloxane copolymer was prepared by hydrogen silylation by Sun Xiuwu et al.^[2] After blending with epoxy resin, they found that when the mass fraction of polyether increased to about 75%, the average particle size of the dispersed phase decreased to less than 1.5 μm , indicating that the compatibility of the copolymer and the epoxy resin was increased.

Hou et al.^[3] used silicone and allyl silicon containing hydrogen based glycidyl ether to carry on a hydrosilylation, then obtained polysiloxane containing epoxy groups, and blended the polymer with bisphenol A-epoxy resin at room



temperature finally. The results show that their compatibility is very good and no phase separation. The scanning electron microscope (SEM) photo shows that the dispersion of polysiloxane in the epoxy resin matrix was more uniform with the increase of the amount of polysiloxane containing epoxy groups. From the viscoelastic spectrum, when the mass ratio of polysiloxane containing epoxy groups and the bisphenol A-epoxy resin is 1: 10, the polysiloxane can be well dispersed in the continuous phase of epoxy resin matrix, and the toughening effect is the best.

Zhou Zhifeng et al. [4] used epoxy resin and hydroxyl terminated polymethylsiloxane (PDMS) to synthesize a compatibilizer, which can make PDMS and epoxy matrix well compatible. The thermal stability of epoxy system is improved, and the thermal stability of the system increases with the increase of PDMS content. When the PDMS content is 10%, the impact strength can be increased to 1.5 times that of the unmodified one.

(2) Using organic silicon coupling agent

Yao Haisong et al. [5] synthesized a series of polymer coupling agents (APCA) as bisphenol A-epoxy resin (EP) modifier. The results showed that APCA could obviously improve the properties of the curing system. Among them, comparing 10 epoxy resin modified with APCA-60 with ten unmodified epoxy resin, the impact strength increased nearly doubled, the elongation increased by 94.55% and the glass transition temperature increased by 5 degrees, which significantly improves the heat resistance and toughening effect.

Cheng Bin et al. [6] took silane coupling agent KH-560 and silicone modified phenolic resin curing agent, blended silicone rubber and epoxy resin, and improved the compatibility of the system at last. The structure of KH-560 is shown in Fig.1:

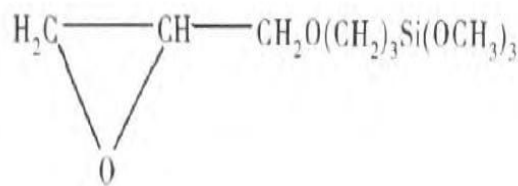


Fig.1 The structure of KH-560

The structure contains groups compatible with silicon rubber and epoxy resin. It can reduce the interfacial tension in the blending, improve the compatibility between resins. Compared with the unmodified epoxy resin, the hardness of the modified samples decreased, but the impact strength and the heat resistance increased.

2.1.2 Copolymerization modification

Copolymerization is based on the reaction of terminal group such as hydroxyl, amino, alkoxy on the organic silicon and epoxy group, hydroxyl in the epoxy resin to generate graft or block copolymer to solve the problem of compatibility, and to introduce a stable and flexible Si-O bond in the curing structure to improve the fracture toughness of the epoxy resin.

(1) Modification of epoxy resin with hydroxyl or alkoxy silicone

Low molecular weight polysiloxane containing alkoxy or hydroxyl groups can react with epoxy resin to produce epoxy resin modified with polysiloxane by grafting or block copolymerization. The reaction can be carried out in 3 ways.



① Dealcoholization of alkoxy in organic silicon with C-OH base in epoxy resin

Li Yinwen et al.^[7] used polymethyl phenyl siloxane (PMPS) grafted and modified epoxy resin (E-20) to analyze the properties of the cured products by infrared spectroscopy (IR) and differential thermal analysis (DSC). The results showed that when m (E-20): m (DC-3074) = 7: 3, the heat resistance of the curing system of chemical modified resin was obviously improved, and at the same time, as the high temperature anticorrosive coating, this modified resin condensate has good film properties.

Su Qianqian et al.^[8] used two butyl tin laurate as catalyst and dimethyl diethoxy silane (DMDES) to modify the bisphenol A-epoxy resin. The results showed that the tensile strength of the organic silicon modified solidified substance reached to 54.07 MPa, the elongation at break reached 11.68% and T_g reached 166.07 °C, not only the mechanical properties of the solidified substance were raised, but also the thermal properties.

② Dehydration of silicone hydroxyl in organic silicon with C-OH base in epoxy resin

Tian Jun et al.^[9] used hydroxyl terminated poly two methyl siloxane and epoxy resin 6101 to react, under the catalytic organic tin salt, then the direct reaction of hydroxyl terminated silicone and hydroxyl in epoxy resin was in S-O-C bond formation. The microstructure of the modified resin showed a two phase separation structure, and the two phase interface was blurred. The dispersion phase among the organic silicon and the epoxy resin formed the interpenetrating transition layer, the compatibility was improved. With the increase of the hydroxyl terminated polymethylsiloxane in the modified resin, the surface energy decreased but the hydrophobicity was improved. The thermogravimetric data showed that the heat resistance of the modified resin was higher than that of the unmodified resin. This is due to the higher bond energy of the Si-O bond on the main chain of the hydroxyl terminated polymethylsiloxane, and the interpenetrating network transition layer strengthens the interaction between two phase.

③ Ring opening reaction of hydroxyl of organic silicon and epoxy group in epoxy resin.

Zheng Yaping et al.^[10] used the hydroxyl of organic silicon and epoxy group in epoxy resin to initiate ring opening reaction to form the stable Si-O bond. In addition, silane coupling agent KH-550 was added as the transition phase to improve their compatibility. The amino and alkoxy of the coupling agent respectively reacted with epoxy, hydroxyl terminated in epoxy resin and hydroxyl in polysiloxane, to produce block structure, improve the compatibility and reduce the stress. Zhang Shun, Xie Jianliang et al.^[11] used triphenyl phosphorus and butyl titanate to catalyze the graft copolymerization of organic silicon Z6018 and E44. The active hydroxyl group in organic silicon Z6018 and the epoxy group of E44 had ring opening reaction under the action of the catalyst, and a new kind of modified resin with good heat resistance and mechanical properties has been obtained.

(2) Modification of epoxy resin with organic silicon with amino

Ming-chun Lee et al.^[12] used the reaction of polydimethylsiloxane with aminopropyl terminated poly and an epoxy resin four functional groups, formed an "island" structure in the resin matrix, improved the modification of T_g , and reduced the internal stress.

Zheng Qinjian et al.^[13] modified epoxy resin (E-44) with synthetic side amino polysiloxane. The results showed that polysiloxane containing the amino groups could effectively toughen epoxy resin, and the greater viscosity of SAPS, the higher impact strength of modified epoxy matrix.

Zhang Bin et al.^[14] compounded the modified epoxy resin by the reaction of polysiloxane containing terminated amino



group and bisphenol A-epoxy resin. The elongation at break of epoxy resin was increased obviously. When the content of organic silicon was 2%, the elongation at break of the composites reached 93%, which was nearly 4 times higher than that of the pure epoxy resin. As for the heat resistance, the heat resistance of the modified epoxy resin increased significantly with the increase of organic silicon content.

(3) Modification of epoxy resin with organic silicon containing siloxane

Tsung-Han Ho et al.^[15] used polydimethylsiloxane with terminal hydroxyl to modify *o*-methyl phenolic epoxy resin with a double bond. The epoxy resin was prepared where polysiloxane particles stably dispersed through hydrosilylation. The results showed that the flexural modulus and thermal expansion coefficient of the modified resin decreased, and the internal stress of the material was reduced. In addition, the T_g of the modified resin was almost not reduced, and the hygroscopicity was improved obviously. It can be used in molding compounds of semiconductor integrated circuits.

Sheng-shu Hou et al.^[16] used DC1107, D4 and DC200 to react and produce polysiloxane containing hydrogen, and then to react with allyl glycidyl ether (AGE) to produce polysiloxane whose side chain containing epoxy group via hydrogenated reaction. The modified resin S (G) was mixed with ordinary epoxy resin (DGEBA) and solidified with Dicyandiamide (DICY). The addition of SG improved the fluidity and thermal stability of the crosslinked network of cured epoxy resin.

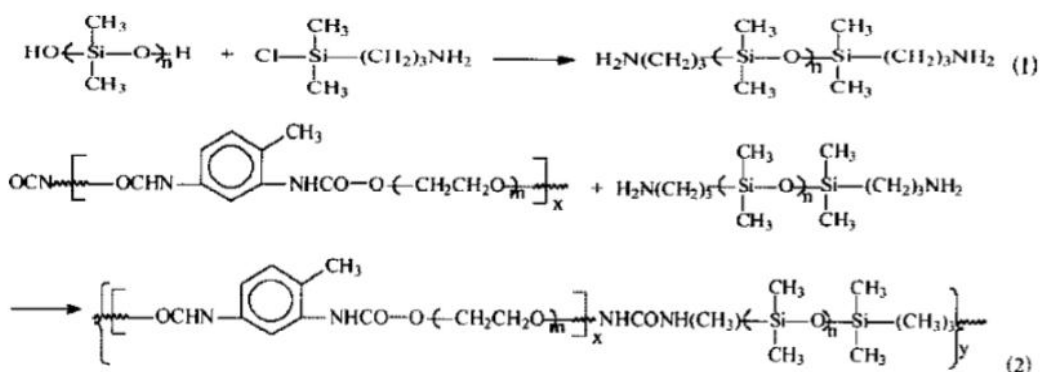
(4) Reaction of organic silicon containing hetero atoms with epoxy resin

Wang Ding et al.^[17] used the reaction of phenyl methyl silicone resin with phenolic epoxy resin to make adhesive. Compared with the burn-in of 200 hours at 100 °C, the shear strength of the adhesive decreased by 7.5% of the burn-in of 200 hours at 300 °C, reaching 12.3 MPa. Peng Ronghua et al.^[18] used boric acid and organic silicon to modify epoxy resin E-42, and toughened with polyvinylbutyral to obtain a good flexibility adhesive. The workpiece which is adhered to can meet the requirements of long-term under 150 °C. Li Yan et al.^[19] produced two kinds of organic silicon with terminal chlorine α , ω -dimethyl polydimethylsiloxane (DPS) and α -chloro polydimethylsiloxane (CPS), by using modified ordinary bisphenol A-epoxy resin (BPAER) and four tetrabromobisphenol A-epoxy resin (TBBPAER). The epoxy group was not consumed in the modification process, and the crosslinking density of the cured resin was also improved, thus the resin was toughened and its heat resistance and impact resistance were improved.

2.2 Synthesis of polyurethane modified with organic silicon and the study on anticorrosive properties

Polyurethane has been widely used in coatings industry due to its excellent properties such as high elasticity, abrasion resistance, embrittlement, abrasion resistance, low temperature resistance and good compatibility and so on. However, polyurethane also has some disadvantages such as poor surface performance, flammability, poor high temperature resistance and aging, which limits its development in some fields^[20]. Organic silicon has good heat resistance, good weatherability, good hydrophobicity, physiological inertia etc., so the excellent properties of the two materials can be integrated to make up for the shortage of polyurethane to meet the various needs of different industries and fields. Polyurethane modified with amino silicone oil was prepared by copolymerization, and the functionalized organic silicon modified polyurethane with better salt spray resistance.

In which, equation 1 represents the synthesis process of amino silicone oil, equation 2 represents the process of amino silicone oil modified polyurethane.



Whether the salt spray test under constant condition or the cyclic corrosion method developed in the later stage, the salt spray corrosion mechanism of the process is basically the same. When the particle settlement of the salt mist attaches to the surface of the material, it quickly absorbs moisture and dissolves into a chloride solution. Under certain temperature and humidity conditions, the chloride solution or the dissociated chloride ion penetrates into the material system through the pores of the paint film, the coating or other materials, resulting in the aging of the material or the corrosion of the metal.

Amino silicone oil can be used for copolymerization modification of polyurethane. Under the same salt spray test environment, the amino silicone oil modified polyurethane coating had better anticorrosion performance on the surface of copper than the single polyurethane coating. In addition, when the salt spray test was carried out, observing the surface of copper sheet coated with polyurethane modified by amino silicone oil, the water droplets on the surface of the copper sheet were spherical. The reason for this phenomenon is that the modified polyurethane contains hydrophobic silicone oil and its surface free energy is lower than single polyurethane coating^[21]. After adding amino silicone to polyurethane, the chain segment of siloxane is migrated and enriched to the surface of the material, which reduces the surface free energy of the modified polyurethane and obstructs the contact between the water and the metal surface. This is the main cause of the improving of salt spray resistance of the modified polyurethane coating.

3. Conclusion

Two kinds of methods of physical blending and graft copolymerization to synthesize epoxy resin modified with organic silicon, and their heat resistance, adhesion, compatibility and toughness of epoxy resin can be improved. Epoxy resin modified with organic silicon is transparent and non-layered latex long-term placement. The corrosion resisting coatings produced by epoxy resin modified with organic silicon have good heat resistance and good chemical resistance. The synthetic process has the characteristics of simple, reliable and little environmental pollution.

Copolymerization of polyurethane with amino silicone oil can greatly improve the corrosion resistance to metal of polyurethane and improve its salt spray resistance. Epoxy resin and polyurethane modified with organic silicon have good prospect in the future.

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