

Preparation and Organic Solvent Resistance of Water Soluble Hydantoin Epoxy/Organic Titanium Chelate Composite Coatings

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Abstract. As worldwide environmental and ecological regulations become strict, water soluble system presents great potential in the new VOC-compliant, high-performance anticorrosive coating systems. In this study, hydantoin epoxy resin (HE) was first synthesized. Then HE/titanium bis(triethanolamine) diisopropoxide (TE) composite resin was obtained by mixing HE and TE at a certain temperature. The structure was characterized by ¹H nuclear magnetic resonance (NMR) and fourier transform infrared spectroscopy (FTIR). The curing behavior and thermal stability were assessed with differential scanning calorimetry (DSC) and thermo gravimetry (TG) analysis. The mechanical properties of the cured coatings were discussed under the corresponding standards. The chemical resistance properties were tested by immersion test. Our study revealed that the HE/TE composite resin was water soluble and could be self-cured by heating. It possessed well thermal resistant properties, excellent physical and mechanical properties, and good chemical resistance, which made it suitable for the surface coating industry.

Introduction

Epoxy resins were widely used as protective coating and adhesive due to their outstanding performances in terms of corrosion protection, chemical resistance and adhesion properties [1]. So far, the majority of the epoxy coatings are formulated with solvents. They release high levels of volatile organic compounds (VOC), which cause serious environment pollution and endanger human health. In order to protect the environment, worldwide environmental and ecological regulations become stricter to limit VOC emissions, resulting in a continuous shift from solvent-borne coating to waterborne coating [2]. Waterborne systems use water as diluting agent and have the advantage of easy cleaning of the equipments in application, which are harmless to environment and human health. Therefore, the study of waterborne epoxy resins has received much attention in recent years, despite their somewhat higher cost and slightly reduced performance [3, 4].

Waterborne systems contain water soluble system and water dispersible system [5-10]. At present, water dispersible epoxy resins coatings have been widely employed as building coatings and wood paints, while their application as anticorrosive coatings for metal is still limited [5, 11]. The chemical resistance of the water dispersible still can't be enhanced to the level of a solvent-based system, which limits its application. For waterborne epoxy/amine coatings, Wegmann *et al* [12] found that the main responsibility for the poor resistance to chemicals lied with an inhomogeneous film structure due to insufficient coalescence during the curing process. While, in the solvent-based film, resin and hardener react chemically to form a 3-dimensional network in a homogeneous phase. Therefore, the water dispersible system was inferior to the solvent-based system in the properties. However, in the water soluble system, the resin and hardener react in a homogeneous phase, which is similar to the solvent system. More over, there need be no surfactants in the water soluble system. Therefore, water soluble system presents great potential in the new VOC-compliant, high-performance anticorrosive coating systems. However, there were few reports on the application of water soluble system in recent years.

Hydantoin epoxy resin (HE) is a new type of special epoxy resin, which is glycidylated hydantoin and its derivatives [13]. It maintains the performance of ordinary epoxy resin. More over, heterocyclic structure of hydantoin makes HE with good electrical isolation, heat resistance, weather resistance and abrasion performance. Therefore, HE was widely used in the fields of electronic packaging materials [14], insulation material [15], antibacterial agent [16] and so on. Titanate has been widely used in paints because of its unique performance. However, titanate is unstable and easy to hydrolysis, so it could not be used in waterborne coatings. However, organic titanium chelates are very stable in water and have been used as curing agents of epoxy resin [17]. Used as curing agents, organic titanium chelates would improve dielectric performance, curing rate, adhesion and mechanical properties of the epoxy resin. Among the organic titanium chelates, titanium bis(triethanolamine) diisopropoxide (TE) is the most commercially valuable.

In the present study, a water soluble epoxy resin system was proposed to prepare HE/TE composite coatings with high organic resistance. The composite resins were characterized by ^1H nuclear magnetic resonance (NMR) and fourier transform infrared spectroscopy (FTIR). The curing behavior, thermal stability and the mechanical properties of the cured coatings were discussed. The chemical resistance properties were tested by immersion tests.

Experimental Methods

Materials. 5,5-dimethyl hydantoin was purchased from Jihua Jiangcheng oil Chemical Co., Ltd., China. Titanium bis(triethanolamine) diisopropoxide (TE) was purchased from Nanjing Capatue Chemical Co., Ltd. Epichloroghyrin, triethanolamine, sodium hydroxide and other chemicals were supplied by Tianjin Kemiou Chemical Reagent Co., Ltd., China and used as received. Distilled water was prepared by Ai Kepu (Aquapro) ultra pure water system.

Preparation of HE. A certain amount of 5,5-dimethyl hydantoin, epichloroghyrin and triethanolamine catalyst were added into a round-bottom flask and stirred vigorously at 90°C for two hours. Then, the temperature was lowered to 60°C and dehydrohalogenation was carried out with dropwise addition of 50wt% sodium hydroxide solution in distilled water. The temperature was kept at $70\text{--}75^\circ\text{C}$ by controlling the drop speed. After the complete addition of sodium hydroxide solution, reaction was allowed for ten minutes more. The excess epichlorohydrin and water were removed by pressure distillation. Finally, the resulting salt was separated and HE was obtained.

Preparation of the HE/TE composite coatings. An aqueous HE solution in a concentration of 60wt% was taken in a beaker. Then, TE (15wt% with respect to HE) was added. Finally, the above mixture was stirred vigorously for one hour at room temperature or 80°C . The obtained HE/TE composite resins at room temperature and 80°C were marked as HE/TE(R) and HE/TE(H) respectively to study the effect of the reaction temperature on the resins and coatings properties.

For preparation of cured coatings, a certain amount of water was added into the HE/TE(R) and HE/TE(H) composite resins and stirred until the viscosity of the mixture was suitable to cast. Galvanized iron sheets were polished successively with fine grade sandpapers and then washed thoroughly by acetone for further use. The aqueous HE/TE composite resin solution was coated onto the treated galvanized iron sheets and dried at room temperature for 1-3 h. All coated samples were cured at 180°C for 2 h in an air-circulating oven. The cured HE/TE(R) and HE/TE(H) composite resins are expressed as HE/TE(R, cured) and HE/TE(H, cured) in this paper, respectively.

Characterization and testing. ^1H NMR spectra of HE were obtained on a Varian machine (INOVA 500 MHz and Infinity plus 300WB, USA) by dissolving the samples in D_2O . FTIR spectra of HE were recorded in a Spectrum 100 FT-IR spectrometer (FTS3000, BIORAD, USA) in the range from 4000cm^{-1} to 400cm^{-1} .

The curing behavior of HE/TE(R) composite resin was assessed with differential scanning calorimetry (DSC) and thermal stability of the HE/TE(R, cured) was assessed with thermo gravimetry (TG) analysis with a simultaneous Thermal Analysis (DSC/DTA-TG, NETZSCH, STA 409 PC Luxx®, Germany) under the nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ from 30°C to 500°C .

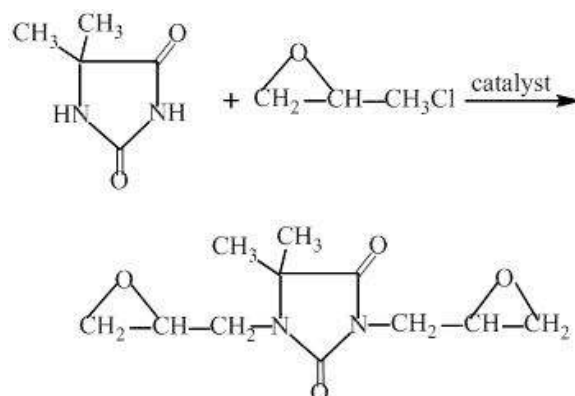
HE/TE(R, cured) and HE/TE(H, cured) were applied on galvanized iron sheets of standard size for physical and mechanical properties. The adhesive force was measured under the GB/T1720-1979 standard. Flexibility was tested according to the GB/T 1731-1993 standard. The impact strength was determined by dropping a dart onto the center of the test specimen from varied drop heights of the Film Impact Tester. The drop heights and the test fail results were recorded as the GB/T 1732-1993 standard. The pencil hardness was determined by pencil test under the GB/T 6739-2006 standard.

The chemical resistance properties of HE/TE composite coatings were determined by the immersion test [18]. Specimens were placed into different glass containers with xylene, acetone, ethanol, dimethylbenzene or diesel and carried out for 50 days at room temperature. After immersion, the visual examination was conducted for deterioration such as blister, cracking spot or spoil.

Results and Discussion

The HE/TE composite resins. Scheme 1 represents the synthesis of HE. The reaction takes place between the imide proton of 5,5-dimethyl hydantoin and epoxy group of epichlorohydrin in the presence of triethanolamine. After dehydrohalogenation with sodium hydroxide, HE was obtained. Fig. 1 represents the ^1H NMR spectra of HE. The peak at $\delta=1.40\text{ppm}$ was assigned to the methyl groups of hydantoin. The peak at $\delta=2.62\text{-}2.92\text{ppm}$ was due to $-\text{CH}_2-$ protons present in the epoxy groups, while the peak at $\delta=3.25\text{ppm}$ can be ascribed to the protons of the $-\text{CH}-$ groups in the epoxy group, leading to the formation of epoxy resin. The peak for protons of $-\text{CH}_2-$ attached directly to N atom of the five-membered heterocyclic ring appeared at $\delta=3.55\text{-}3.88\text{ppm}$. However, there were no peaks at $\delta>5.5\text{ppm}$ for $-\text{NH}-$ protons, which also indicated the reaction of hydantoin and epichlorohydrin. FTIR spectra of HE is shown in Fig. 2. The bands at 2982cm^{-1} and 2936cm^{-1} were due to the $-\text{C}-\text{H}$ asymmetric and symmetric stretching absorption of the $-\text{CH}_3$ groups in hydantoin ring. The bands at 1697cm^{-1} and 1765cm^{-1} could be ascribed to the $-\text{C}=\text{O}$ stretching vibration absorption. The band at 1449cm^{-1} was attributed to the $-\text{C}-\text{N}$ stretching vibration. The presence of a characteristic band 850cm^{-1} was the evidence for the formation of HE resin. More over, the bands at $1550\text{-}1530\text{cm}^{-1}$ for $-\text{N}-\text{H}$ plane bending vibration absorption didn't appear, which further indicated the reaction of the imide proton of 5,5-dimethyl hydantoin and the epoxy group of epichlorohydrin. In conclusion, the ^1H NMR spectra and FTIR spectra proved that HE was successfully synthesized.

The obtained HE reacted with TE at room temperature or 80°C to prepare HE/TE composite resin. Fig. 2 also shows the FTIR spectra of the composite resins and the cured ones. It could be seen that the band at about 850cm^{-1} of epoxy group of HE/TE(R) and HE/TE(H) became weaker than that of HE. The epoxy group absorption peak of HE/TE(H) was weaker than that of HE/TE(R), which indicated that the reaction of HE and TE was carried out more completely by heating. The weaken of hydroxyl group of HE/TE(R) and HE/TE(H) also indicated the reaction of HE and TE. After cured, the hydroxyl and epoxy groups disappeared. It was proposed that the composite resin could be cured by heating above certain temperature without any curing agent. Reaction temperature took no effect on the cured resin. Therefore, we choose the HE/TE(R) composite resin for the DSC and TG characterizations.



Scheme 1 Synthesis of HE.

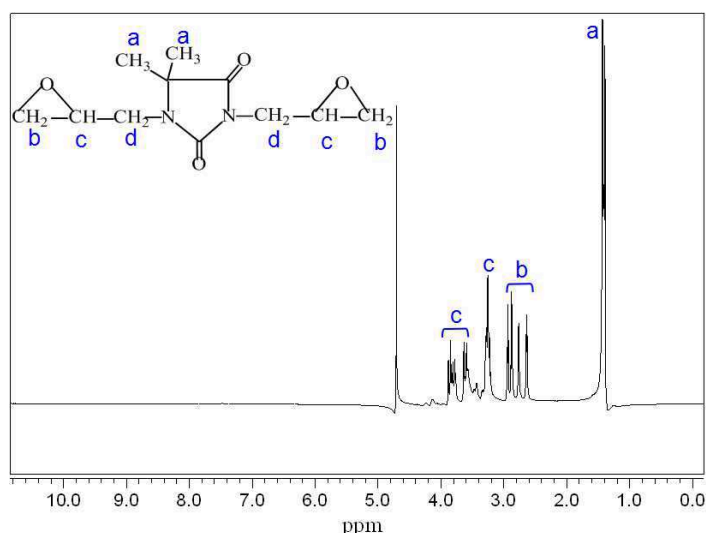


Fig. 1 ^1H NMR spectra of HE.

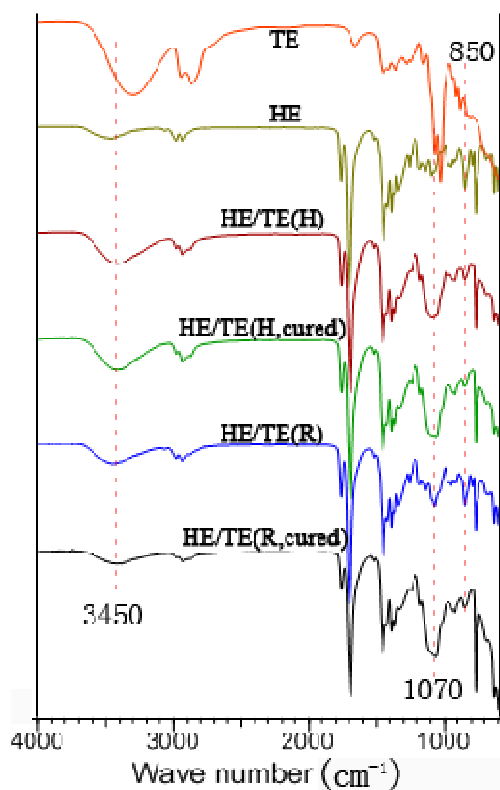


Fig. 2 FTIR spectra of TE, HE, HE/TE(H), HE/TE(H, cured), HE/TE(R) and HE/TE(R, cured).

Curing behavior and glass transition of HE/TE resins. It is necessary to study the curing behavior in order to obtain coatings with excellent properties. DSC which measures the heat flow from the reacting system is a very convenient tool to study the cure behavior of resins [19, 20]. Fig. 3 shows the curing curves of HE/TE(R) obtained by DSC. A broad exothermic peak appeared at about 129°C , which may be regarded as the onset of the cure reaction for HE/TE(R) resin. Tg of the HE/TE(R, cured) were examined by DSC. As shown in Fig. 4, Tg was found to be about 274°C , indicating the excellent heat resistance. There was only one thermal transition in the DSC curve in the temperature from 30°C to 500°C . Therefore, the composite resin was a homogeneous phase.

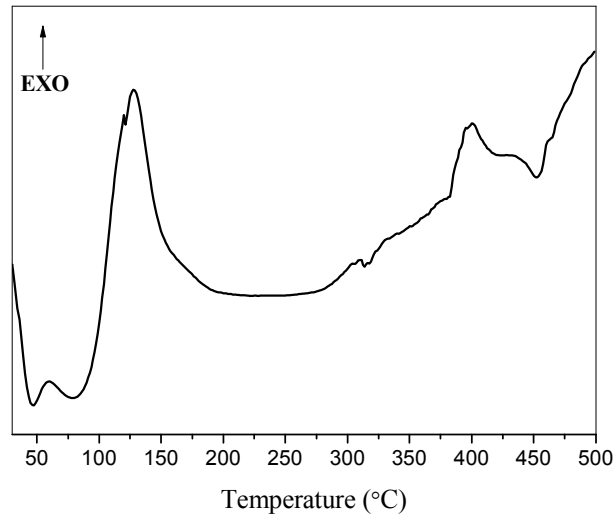


Fig. 3 Curing study of HE/TE(R)

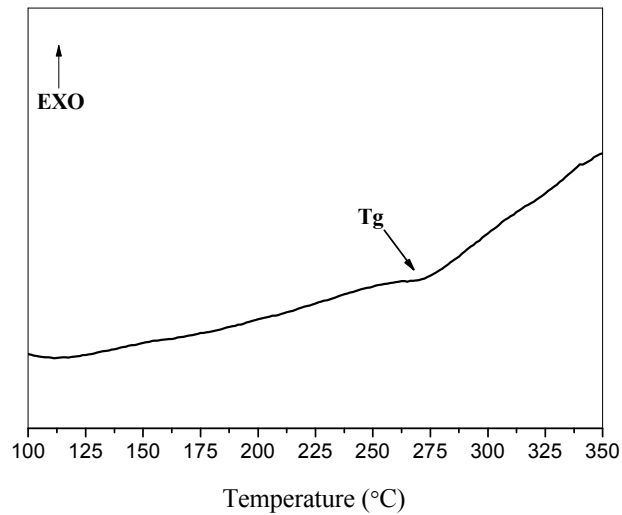


Fig. 4 DSC curves of HE/TE(R, cured)

Thermal properties. The thermal degradation behavior of HE/TE(R, cured) is shown in Fig. 5. The 5 wt% and 10 wt% losses occurred at 326°C and 353°C, respectively. Therefore, the degradation of the cured composite resin started at about 300°C. The HE/TE(R, cured) coating kept its weight constant when the temperature was below 300°C, which indicated that the coatings exhibited well thermal resistant properties.

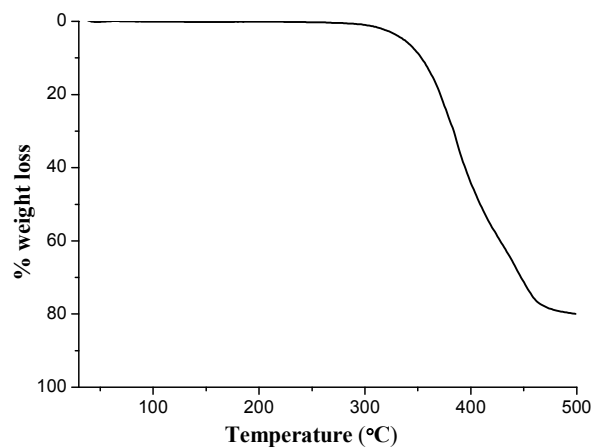


Fig. 5 Weight loss curves of HE/TE(R, cured) resin by TGA

Physical and mechanical properties. The physical and mechanical properties of HE/TE(R, cured) and HE/TE(H, cured) are shown in Table 1. It can be seen that HE/TE(R, cured) and HE/TE(H, cured) exhibited the same physical and chemical properties. Both of them possessed excellent adhesion, flexibility, impact endurance and hardness.

Table 1 Physical and mechanical properties of HE/TE(R, cured) and HE/TE(H, cured) composite coatings

	HE/TE(R, cured)	HE/TE(H, cured)
Adhesive force (grade)	1	1
Flexibility (mm)	≤ 1	≤ 1
Impact strength (kg.cm)	≥ 50	≥ 50
Scratch hardness	2H	2H

Chemical resistance properties. Chemical resistance test was used to find the ability of the HE/TE(R, cured) and HE/TE(H, cured) composite coatings to withstand exposure to organic chemicals. Examinations of the chemical resistance were performed by immersing the coatings in various chemical solvents such as xylene, acetone, ethanol, dimethylbenzene or diesel. After immersion, there were no signs of cracking spots, blisters, or other indications of solvent attack observed on all the films. The results indicated that the HE/TE composite coatings possess fairly good chemical resistance.

Conclusions

HE resin was successfully synthesized. HE/TE composite resin was then developed by mixing HE and TE at a certain temperature. The HE/TE composite resin was water soluble and could be self-cured by heating. DSC of the composite resin showed that it could be self-cured at high temperature and Tg of the cured HE/TE resin was about 274°C. TGA analysis showed that the composite coatings exhibited well thermal resistant properties, which showed its potential in application of heat-resisting paint. In addition, the composite resin possessed excellent physical and mechanical properties and good chemical resistance, which make it suitable for the surface coating industry.

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