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Characterization and properties of epoxy resin (E-20) modified with silicone intermediate RSN-6018

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ABSTRACT

In this research, a series of epoxy resin modified with organosilicone intermediate RSN-6018 (RE) were prepared through a condensation reaction between the C—OH of bisphenol-A type epoxy resin and the Si—OH of organosilicon intermediate. These resins, having solid content up to 80 wt.%, could be cured at room temperature by a polyamide curing agent to yield transparent coatings. Chemical structures of the products were characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). The morphology of fractured surfaces of the cured coating films was studied by scanning electron microscopy (SEM). The thermal properties of the cured coatings were evaluated by thermogravimetric analysis (TGA). The results indicated that film was stable while temperature below 348.96 °C, and the film hardness could be up to 6H when the content of organosilicon was 44.2%. Differential scanning calorimetry (DSC) analysis tests displayed that the glass transition temperature (Tg) of cured coatings decreased when the ratio of organosilicon intermediate increased.

1. Introduction

Organic silicon resin is a kind of high performance polymer with the structure of Si—O—Si in its molecular main chain. It has excellent heat resistance because the Si—O bond energy, 460 kJ/mol, is far higher than that of the C—C, 345 kJ/mol. Additionally, it has superior thermo-oxidative stability, excellent moisture resistance, low surface energy, outstanding weather ability, good hydrophobicity, and so on. These are all important properties for its use as heat resistance and anti-corrosion coatings [1–4].

However, these potential applications of organic silicone resin are limited by its high curing temperature and long curing time. In addition, the poor solvent resistance and poor mechanical properties also make it easy to be destroyed in the process of application [5–9]. In light of these problems, a great deal of scientific researches have been conducted, such as synthetization of new type silicone resin and modification of silicone resin [10–13]. Among the numerous approaches to improve the performance of the silicone resin, the method of introducing epoxy resin into the silicone resin network have drawn much attention and turned out to be an effective way, because the epoxy resin has excellent mechanical, bonding and chemical properties. For instance, Weng et al. [14] synthesized epoxy-silica hybrids material from tetraethoxysilane by using glycidoxypropyl-methyldiethoxysilane to provide covalent bonds between epoxy resin and silicone resin. The coupling agent improved the thermal properties of hybrid materials, especially when its amount was 5 wt.%. Epoxy-grafted silicone have been prepared and characterized for their thermo-mechanical properties by Ochi et al. [15]. The storage modulus in the rubbery region increased with the hybridization of the silica network.

However, most of epoxy modified organosilicon resins have to be cured under high temperature, and the content of organosilicon is relatively low. In this work, we synthesized the epoxy-modified silicone, and it could be cured by curing agent at room temperature, and the content of organosilicon could reach to 44.2%. The epoxy-modified silicone resin was characterized by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR). The morphology of the cured coatings was characterized by scanning electron microscopy (SEM). Besides, mechanical properties of the coatings were evaluated, and the thermogravimetric analysis (TGA) was used to assess the heat resistance of the coatings.

2. Materials and methods

2.1. Materials

Bisphenol-A type epoxy resins (E-20, shown in Table 1) was supplied by Jiangsu Wuxi Resin Plant, China. Organosilicon Intermediate (RSN-6018, shown in Table 2) was purchased from Dow Corning, US. Dibutyltin dilaurate (DBTDL), which was used as catalyst directly, was purchased from Chengdu Chemical Reagent Company, China.

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Table 1
The parameters of epoxy resin E-20.

Code	State	Functional group	Epoxide equivalent weight (g/equiv)	M_w
E-20	Solid	Hydroxy epoxy	450–00	900–1100

Table 2
The parameters of RSN-6018 organosilicon intermediate.

Code	State	Functional group	Content of functional group(wt.%)	Type of substitute	M_w
RSN-6018	Solid	Hydroxy	0.13	Phenyl	792

Table 3
The parameters of polyamide 650.

Code	State	Functional group	Amine value (g/equiv)	M_w
Polyamide 650	Liquid	Amido	200–240	600–1000

Cyclohexanone and Butyl acetate, which were used as solvents, were purchased from Tianjing Damao Chemical Reagent Company, China. The curing agent (polyamide 650, shown in Table 3) was purchased from Jiangsu Wuxi Resin Plant, China. All of the materials utilized in this study were used directly without further purification.

2.2. Preparation of epoxy resin modified with organosilicone intermediate RSN-6018 (RE)

The preparation of RE was achieved via one step procedure. The formulation was illustrated in Table 4. A certain amount of RSN-6018, E-20, 0.2 wt.% DBTDL, cyclohexanone and butyl acetate were added into a 250 mL four-neck rounded-bottomed flask, which was equipped with mechanical stirrer, thermometer. Then, the mixture was heated to 140–150 °C. The reaction was maintained for 3–4 h with vigorously stirring. The specific reaction process was depicted in Fig. 1.

2.3. Curing of the RE

A calculated amount of curing agent polyamide 650 was added to the RE. The weight of curing agent (W_{CA}) was calculated as follows:

$$W_{CA} = \frac{W_{EP} \times A}{EEW}$$

Where W_{EP} was the weight of the epoxy resin, A was the amine value of the curing agent. Then, the mixtures were blended by constant vigorously stirring at ambient temperature until they become homogenous liquid. Subsequently, the mixtures were poured in preformed molds for curing at room temperature for 7 days. After that all resin samples were dried under vacuum at room temperature for 24 h.

2.4. Characterization

2.4.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectrum was recorded between 4000 cm^{-1} and 400 cm^{-1} by using a Nicolet 380 FTIR spectrophotometer (Nicolet Instrument Co., USA). Samples were prepared by dispersing the dried samples in KBr and compressed the mixtures to form disks.

Table 4
Formulation of organosilicon intermediate (RSN-6018) modified with epoxy resin (E-20).

Sample code	RSN-6018 (wt.%)	E-20 (wt.%)	Solvent (wt.%)
RE-16	16.5	83.5	20
RE-21	20.9	79.1	20
RE-28	28.4	71.6	20
RE-44	44.2	55.8	20

2.4.2. Nuclear magnetic resonance (NMR)

NMR measurements were performed on a DRX-400 400 MHz NMR spectrometer (Bruker, Germany) to obtain ^1H NMR spectra at 25 °C. The samples were dissolved in dimethylsulfoxide (DMSO).

2.4.3. Epoxy equivalent weight (EEW)

EEW of the RE was determined by using the hydrochloric acid/acetone method according to GB/T 1677-2008 standard. The average value of EEW was obtained by testing five samples (1.0–2.0 g).

2.4.4. Scanning electron microscopy (SEM)

The morphology of the fracture surface was observed by using a scanning electron microscope (JSM-5900, Japan) at an accelerating voltage of 10 kV. The surfaces of all the samples were coated with gold to enhance conductivity and prevent charging.

2.4.5. Differential scanning calorimetry (DSC)

The thermal property of RE films was measured by using a differential scanning calorimeter analyzer (TA-Q20, USA). The cured RE films (3.0–8.0 g) hermetically sealed in an aluminum pan were heated up to 180 °C with a heating rate of 10 °C/min and kept for 3 min to keep a consistent thermal history for the melting process. And then, the samples were cooled to room temperature at a cooling rate of 10 °C/min.

2.4.6. Thermogravimetric analysis (TGA)

TGA was performed by using a thermogravimetric analyzer (TG 209F1, Germany) under dry nitrogen gas with a flow rate of 60 mL/min to investigate the thermal stability of the cured RE films. The relative mass loss of the samples was recorded from 30 to 800 °C, and the profiles were recorded at a heating rate of 10 °C/min.

2.4.7. Adhesion properties

The adhesion properties of the coatings were determined by the cross-cut tester method according to GB/T 9286-1998 standard. The substrate used in this method was Q235 plain carbon steel and the size was 1 × 100 × 100 mm^3. The average value of the adhesion was taken from five samples (25 μm).

2.4.8. Pencil hardness

The pencil hardness of the films were measured by pencil test according to GB/T 6739-2006 standard. The substrate used in this method was Q235 plain carbon steel and the size was 1 × 100 × 100 mm^3. The average value of the pencil hardness was taken from five samples (25 μm).

3. Results and discussion

3.1. Chemical structure

FTIR spectra for epoxy-modified silicone and unmodified organosilicon intermediate are illustrated in Fig. 2a and b, respectively. The occurrence of the condensation reaction can be detected efficaciously by comparing the infrared spectra of them. The disappearance of characteristic peak at 3398 cm^{-1} of −OH and the appearance of characteristic peak at 910 cm^{-1} of the epoxy ring [16–18] in Fig. 2a are powerful evidence that the positive chemical reaction happens between organosilicon intermediate and epoxy resin. And the existence of the absorption peak of oxirane group at 910 cm^{-1} can also prove that the oxirane group in E-20 doesn't participate the grafting reaction. Besides, in Fig. 2a, two new distinctive absorption peaks at 1508 cm^{-1} and 1238 cm^{-1} are observed, which confirm the presence of Si-C_6H_5 and Si-