



A self-curing, thermosetting resin based on epoxy and organic titanium chelate as an anticorrosive coating matrix for heat exchangers: Preparation and properties



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ABSTRACT

A self-curing, thermosetting resin containing epoxy groups and organic titanium chelate bonds was synthesized by varying the concentrations of bisphenol A epoxy resin (EP) and diisopropoxy-bis ethylacetato titanate (SG). The structural characterizations via Fourier transform infrared spectroscopy and ^{13}C nuclear magnetic resonance confirmed the successful preparation of the self-curing, thermosetting EP-SG resin. The storage stability of the EP-SG resin was determined by measuring the change in viscosity at 50 °C. The curing behavior and thermal stability were assessed via differential scanning calorimetry and thermo-gravimetric analysis. The mechanical properties of the cured coatings were discussed in the context of the corresponding standards. The chemical resistance was tested using an immersion test. Our study revealed that the EP-SG resin has very good storage stability and can be cured via heating without the use of any curing agents. This advantage avoids the issues of non-uniformity, bubbles, and incomplete solubility of the curing agents in the epoxy resins. The resin possesses good thermal resistance, excellent physical and mechanical properties, and good chemical resistance, which makes it suitable for use as a heavy-duty coating for heat exchangers.

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1. Introduction

Heat exchangers play a very important role in petrochemical refineries. They are used in various processes including conversion, utilization, and recovery of thermal energy [1]. Corrosion protection is critical for heat exchangers since they are frequently exposed to severe conditions and are costly to maintain [2–4]. Thus, there is a commercial interest in reducing or avoiding corrosion of heat exchangers. Heat exchangers used in the petroleum industry are typically made of low-carbon steel, which is prone to corrosion and requires periodic replacement. To reduce replacement costs, high-nickel alloys and stainless steels are commonly used in place of carbon steel. However, they are much more expensive than low-carbon steel, which limits their range of application [5]. Once inexpensive carbon steel tubes are coated with a low-cost, thermally conductive coating that provides corrosion resistance equal to that of high-grade alloy steels, the capital cost of geothermal heat exchangers can be reduced considerably [6]. Naturally, some attention has been paid to the development of corrosion-resistant

coatings for carbon steel exchangers. For example, Holberg et al. [7] prepared urea-siloxane hybrid coatings from a dipodal diurea silane and methyltriethoxysilane via the sol-gel method. These coatings combine corrosion protection with scratch and solvent resistance in a single layer. They also enable the incorporation of polydimethylsiloxane (PDMS) to achieve repellent properties. The coating was applied to plate heat exchangers mounted on North Sea oil platforms in order to prevent crude oil-derived fouling. Sugama et al. [8,9] designed and developed several poly(phenylenesulfide)-based coating systems aimed at extending the useful lifetimes of the carbon steel heat exchanger tubes used in geothermal binary-cycle power plants operating at temperatures up to 160 °C. In addition, a fluoropolymer and a hybrid epoxy/fluoropolymer resin were studied for their potential use in preventing corrosion of the carbon steel pipelines used in the petroleum industry [5]. However, to the best of our knowledge, nearly all of the anticorrosion coatings for heat exchangers are multi-component systems, which require a curing agent for crosslinking. Thus far, no single-component, self-curing coating for heat exchanger anticorrosion protection has been reported.

Epoxy resins, a very important class of thermosetting polymers, are widely used as protective coatings and adhesives due to their outstanding performance in terms of corrosion protec-

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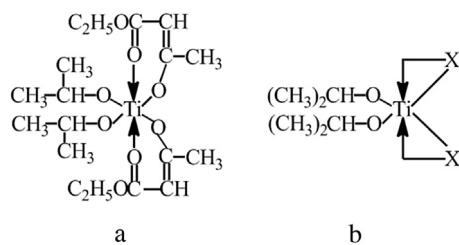


Fig. 1. (a) Molecular structure and (b) skeleton symbol of SG.

tion, chemical resistance, and adhesion [10,11]. Synthetic resins typically require curing agents with functional groups such as hydroxy groups, carboxyl groups, or amino groups for crosslinking. Unfortunately, non-uniformity and insolubility, which cause coating defects, are unavoidable in two-component systems because of differences in the solubility parameters of the epoxy resin and curing agents [12]. The importance of avoiding coating defects is clear: non-defective anticorrosive coatings may have lifetimes of up to 20 years. In contrast, the lifetime of a coating that contains physical damage is much shorter. In addition, the properties and quantities of the curing agents also affect the final properties of the crosslinked resin [13]. Single-component, self-curing epoxy resin coatings have gained attention because of their long pot life, convenience, and ability to cure without an agent. Chen et al. [14] designed a self-curing system of amino-terminated and carboxyl-containing polyurethane and a carboxyl-containing epoxy resin with a latent curing agent in the water phase. However, this self-curing system requires two components and a latent curing agent. Mikroyannidis [15] synthesized a new series of resins, including eight structurally different, self-curing epoxy compounds with azomethine linkages. Free carboxy, amino, and phenolic hydroxy groups can be found in glycidyl ethers and esters, and can thermally crosslink without the presence of a curing agent. Huang et al. [12] synthesized a self-crosslinking compound with both epoxy groups and anhydride groups from tung oil fatty acids. However, trace amounts of a tertiary amine were needed for self-crosslinking. Without using any external crosslinking agents, Patel et al. [16] developed novel, self-curable, cathodically depositable coatings from glycidyl functional epoxy ester-acrylic graft co-polymers. The coatings showed good overall performance, which supports their use in the coating industry.

Over the past thirty years, extensive research on the use of metals and their salts in the formulation of epoxy resin systems has been carried out. This has included the use of organo-transition metal complexes as catalysts for epoxy resins when co-cured with amines, anhydrides, and phenolics [17]. Organo-transition metal complexes have also been added to improve physical properties such as adhesion, flexural strength, fracture toughness, water adsorption, and heat resistance [17]. Titanium alkoxides are superb catalysts for crosslinking of epoxides [18]. Diisopropoxy-bis ethylacetoacetato titanate (SG) has two isopropoxy groups and two ethylacetoacetato ligands. SG is primarily used to improve the heat, chemical, and water resistances of printing inks, paints, coatings, and other products.

Our goal is to prepare a thermally self-curing paint with a long storage life for the prevention of heat exchanger corrosion in petrochemical refineries. In the present study, a self-curing bisphenol A epoxy resin, EP-SG, was synthesized using different molar concentrations of EP and SG. This EP-SG resin contains free hydroxy, epoxy, and titanium chelate groups, which can be thermally crosslinked without the addition of a curing agent or catalyst. The polymerization mechanism and curing behavior of the EP-SG resin were investigated via Fourier transform infrared spectroscopy (FTIR), ^{13}C nuclear magnetic resonance (NMR), and gel permeation chro-

matography (GPC). The storage stability of the EP-SG resin was studied by detecting changes in the kinematic viscosity of the solution. Moreover, the thermal, physical, and chemical properties of the cured EP-SG coatings were also evaluated via various techniques.

2. Materials and methods

2.1. Materials

Bisphenol A epoxy resin (EP) was supplied by Jiangsu Sanmu Co., Ltd., China. Diisopropoxy-bis ethylacetoacetato titanate (SG) was purchased from the E.I. Du Pont Company, USA. Xylene, isopropanol and other chemicals were supplied by Tianjin Kemiou Chemical Reagent Co., Ltd., China and used as received.

2.2. Preparation of the self-curing EP-SG resin

First, a certain amount of EP was dissolved in a xylene/isopropanol solvent mixture to obtain a 55 wt% solution. A quantity of the above EP solution was added to a three-necked, round-bottomed flask equipped with a mechanical stirrer, thermometer, and circulating water condenser. Then, the required SG was added to the round-bottomed flask. Finally, the above mixture was stirred vigorously for two hours at either room temperature or 80°C . The resulting EP-SG resins prepared at room temperature or 80°C were marked as EP-SG (R) and EP-SG (H) respectively, to study the effect of the reaction temperature on the resins and their coating properties. EP-SG resins with SG concentrations of 5%, 15%, 30%, and 50% with respect to EP were marked as EP-SG (5% SG), EP-SG (15% SG), EP-SG (30% SG), and EP-SG (50% SG), respectively.

2.3. Preparation of cured EP-SG coatings

For preparation of cured EP-SG coatings, a certain amount of the xylene/isopropanol solvent mixture was added to the EP-SG resin and stirred until the viscosity of the mixture was suitable for casting. Galvanized iron sheets were polished with successively fine grades of sandpaper and then washed thoroughly with acetone before further use. The above EP-SG resin solution was coated onto the treated galvanized iron sheets and dried at room temperature for 1–3 h, until the surfaces of the coatings were dry. Then, all coated samples were cured at 160°C for 2 h in an air-circulating oven. Dried, uncured EP-SG coatings were marked as EP-SG (uncured) and cured EP-SG coatings were marked as EP-SG (cured).

2.4. Characterization

FTIR spectra were recorded in a Spectrum 100 FTIR spectrometer (FTS3000, BIORAD, USA), in the range of 4000 cm^{-1} – 400 cm^{-1} . The solid-state ^{13}C NMR spectra were recorded on a JNM-ECA400 (JEOL Co. Ltd., 100 MHz). The EP-SG (uncured) and EP-SG (cured) resins were pulverized into powder and put into zirconium sample tubes. The ^{13}C NMR spectra were characterized using the CP/MAS method.

The weight average (M_w) molecular weights and molecular weight distributions (PDI) of EP and the EP-SG resins were determined via gel permeation chromatography (GPC). Samples were dissolved in tetrahydrofuran and filtered with a $0.22\text{ }\mu\text{m}$ filter. GPC measurements were carried out at a flow rate of 1 mL min^{-1} and a temperature of 35°C using polystyrene standards for calibration.

A Tu-4 cup was used to measure the viscosity of the EP-SG resin solution under isothermal conditions. The EP-SG resin solution was placed in a water bath at 25°C for 2 h and its original viscosity was measured. Then, the resin was placed into an air-circulating oven at 50°C . At preset time points, the sample was removed and cooled to 25°C so that its viscosity could be measured. The storage stability

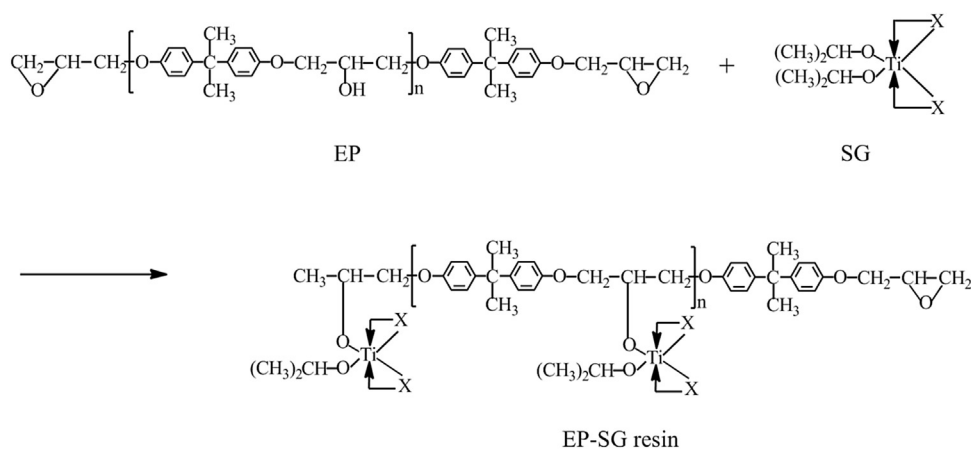


Fig. 2. The synthesis route for the EP-SG resin.

of the EP-SG resin solution was characterized by measuring the changes in its viscosity over time.

In order to observe the reaction process, determine the thermal stability of the coating, and find an ideal curing temperature, the curing behavior and thermal stability of the EP-SG composite resin were assessed via differential scanning calorimetry (DSC) and thermo-gravimetric (TG) analysis with simultaneous thermal analysis (DSC/DTA-TG, NETZSCH, STA 409 PC Luxx®, Germany) under a nitrogen atmosphere, at a heating rate of $10^{\circ}\text{C min}^{-1}$, in the range of 30°C – 500°C .

EP-SG (cured) coatings were applied to galvanized iron sheets of standard sizes so that their physical and mechanical properties could be measured. Flexibility was tested using the GB/T1731-1993 standard. Impact strength was measured using an impact testing machine according to the GB/T1843-2008 standard. The samples were tested using a cantilever beam impact testing machine (Chengde Precision Tester XC-22, China). The adhesive force was measured using the GB/T1720-1979 standard.

Water resistance was measured in pure, boiling water and boiling seawater. Carbon steel bars 100 mm long and 10 mm wide were polished with successively fine grades of sandpaper, and then washed thoroughly with acetone before further use. Following the GB/T1727-1992 standard, the EP-SG resin solution was dip-coated onto the treated carbon steel bars and dried at room temperature for 1–3 h. Then, the coated samples were cured at 160°C for 2 h in an air-circulating oven. All samples were about $180\ \mu\text{m}$ thick. The samples were immersed in pure, boiling water or boiling seawater at atmospheric pressure for 8 h, after which the temperature was reduced to room temperature and maintained for 16 h.

The chemical resistances of the EP-SG coatings were determined via the immersion test. Coated carbon steel bars were placed into different glass containers with various media such as a 10 wt% sodium hydroxide (NaOH) solution, 5 wt% hydrochloric acid (HCl) solution, 5 wt% sulfuric acid (H_2SO_4) solution, xylene, toluene, acetone, diesel, and gasoline, and allowed to sit for 6 months at room temperature. After immersion, a visual examination was performed to detect deterioration such as blistering, cracking, or spoiling.

3. Results and discussion

3.1. Synthesis of the EP-SG resin

The chemical structure and skeleton symbol for SG are shown in Fig. 1. The synthesis route used to make the EP-SG resin is shown in Fig. 2. The ethyl acetoacetate group in SG is stable at room temperature. In the reaction between EP and SG, the hydroxyl and epoxy groups in EP react with the isopropoxy group of SG. To investigate

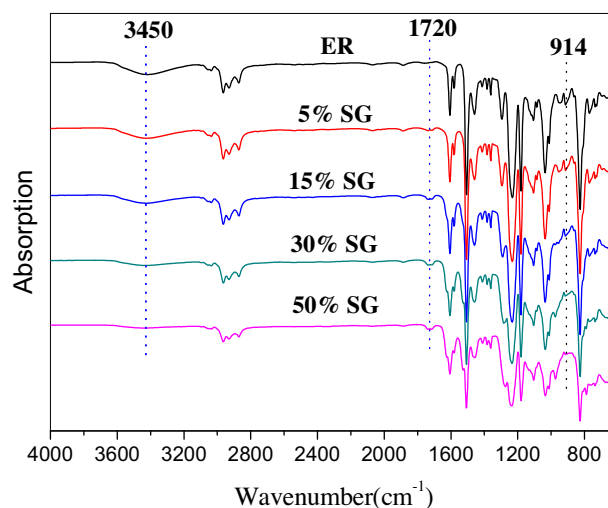


Fig. 3. FTIR spectra of EP and EP-SG resins with varying concentrations of SG.

the reaction mechanism, the structures of the EP, SG, and EP-SG resins were characterized.

Fig. 3 shows the FTIR spectra of EP and EP-SG resins with different concentrations of SG, synthesized at 80°C . In the EP spectrum, characteristic peaks at $3450\ \text{cm}^{-1}$ and $914\ \text{cm}^{-1}$ were assigned to the hydroxyl and epoxy groups, respectively. In the spectrum of the EP-SG resin, the characteristic peaks at $3450\ \text{cm}^{-1}$ and $914\ \text{cm}^{-1}$ decrease as the SG content increases, suggesting that both the hydroxyl and epoxy groups react with SG. In addition, the FTIR spectrum of the EP-SG resin contains a small peak at $1720\ \text{cm}^{-1}$, which represents a characteristic $\text{C}=\text{O}$ absorption peak that has shifted to a lower wavenumber because of the effect of double bonds. This indicates that the chelating ligand, an ethyl acetoacetate group, did not participate in the reaction between EP and SG. Therefore, it is proposed that the hydroxyl and epoxy groups in EP reacted with the isopropoxy group in SG to produce the EP-SG resin, and that the chelating ligand did not react.

In order to study the reaction and curing mechanism of the EP-SG resin, 15% SG was added to the EP resin and the reaction was performed at both room temperature and 80°C . The resulting materials were marked as EP-SG (15% SG, R) and EP-SG (15% SG, H), respectively. Fig. 4 shows the FTIR spectra of EP, EP-SG (15% SG, R), EP-SG (15% SG, H), and cured EP-SG (15% SG, H). There were no significant differences between the EP-SG (15% SG, R) and EP-SG (15% SG, H) samples. After the EP-SG (15% SG, H) resin was cured, the epoxy and hydroxyl group peaks at 910 and $3450\ \text{cm}^{-1}$,

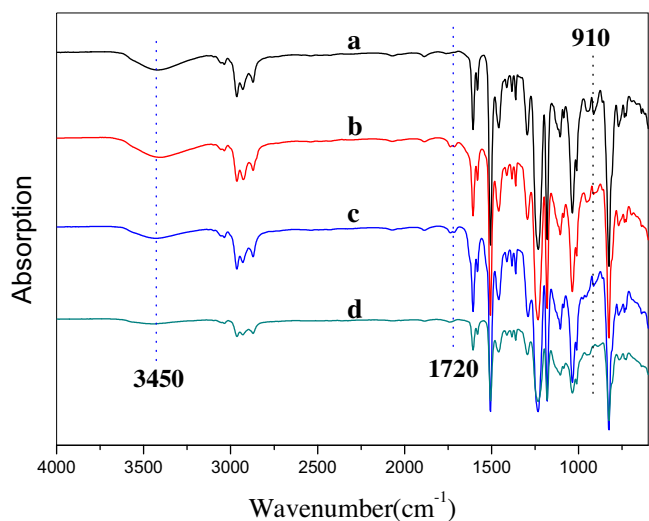


Fig. 4. FTIR spectra of samples [(a) EP, (b) EP-SG (15% SG, R), (c) EP-SG (15% SG, H), and (d) cured EP-SG (15% SG, H)].

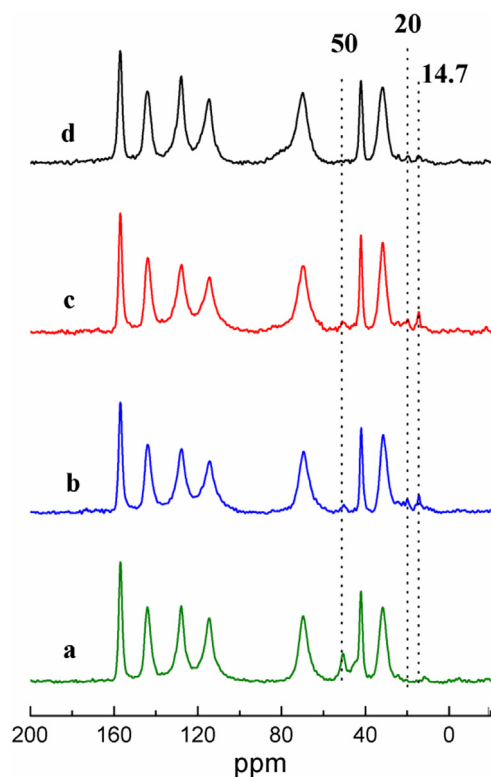


Fig. 5. ^{13}C CP/MAS NMR spectra of samples [(a) EP, (b) EP-SG (15% SG, R), (c) EP-SG (15% SG, H), (d) cured EP-SG (15% SG, H)].

respectively disappeared. Critically, the ethyl acetoacetate peak at 1720 cm^{-1} also disappeared. This suggests that a reaction occurs between the remaining hydroxyl and epoxy groups in the EP structure and the ethyl acetoacetate group in the SG structure, leading to the crosslinking of the EP-SG resin.

The structures of the EP, EP-SG (15% SG, R), EP-SG (15% SG, H), and cured EP-SG (15% SG, H) resins were also confirmed via ^{13}C NMR, as shown in Fig. 5. The signal observed at 50 ppm is due to the epoxy group in the EP structure. The peak at 50 ppm decreases significantly in the spectra of the EP-SG (15% SG, R) and EP-SG (15% SG, H) resins, suggesting that the epoxy resins participate in polymerization. In addition, the signals observed at 14.7 and 20 ppm are

Table 1
Relative molar masses of the EP and EP-SG resins.

Remarks	M_w	PDI
EP	1661	1.57
EP-SG (15% SG, R)	2410	2.15
EP-SG (15% SG, H)	2427	1.99

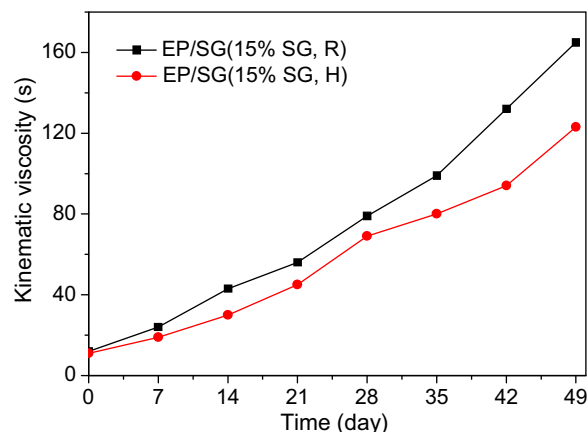


Fig. 6. Change in the kinematic viscosity of the EP-SG (15% SG, R) and EP-SG (15% SG, H) resins.

due to methyl groups adjacent to the double bonds in the ethyl acetoacetate group, which indicates that the ethyl acetoacetate group in SG does not take part in the reaction between EP and SG at either room temperature or 80°C . It is likely that the isopropoxy group in the SG structure participates in the polymerization. After the EP-SG (15% SG, H) resin is cured [Fig. 5(d)], the peak from the epoxy group disappears completely, while the signals from the methyl groups adjacent to the double bonds in the structure of the ethyl acetoacetate group decrease significantly. This is because of the polymerization between the epoxy and ethyl acetoacetate groups. However, it is suggested that addition of 15% SG causes part of the ethyl acetoacetate group to not react. Therefore, there were excess active groups and the signals for the methyl groups do not completely disappear.

The molecular weights (M_w) of the EP, EP-SG (15% SG, R), and EP-SG (15% SG, H) resins were measured via GPC and are shown in Table 1. The original M_w of EP is about 1661. After polymerization at room temperature, the M_w of EP-SG (15% SG, R) increases to 2410. The M_w of EP-SG (15% SG, H) synthesized at 80°C is 2427, which is slightly higher than that of EP-SG (15% SG, R). However, compared to EP-SG (15% SG, R), the molecular weight distribution of EP-SG (15% SG, H) is narrower, indicating that EP and SG react more completely at 80°C .

In conclusion, the hydroxy and epoxy groups in the EP structure reacted with the isopropoxy group in the SG structure at a certain temperature, producing the EP-SG resin. The ethyl acetoacetate group was stable. At high temperatures (e.g. 160°C), the ethyl acetoacetate group in the SG structure was broken and new reactive groups were formed. The new reactive groups could react further with the hydroxy or epoxy groups from EP which did not react during synthesis, leading to the crosslinking of the EP-SG resin.

3.2. Storage stability of the EP-SG resin

The resin's viscosity change reflects its stability in storage. Once its viscosity is high enough, the resin begins to cure and can no longer be used. The viscosity changes of the EP-SG (15% SG, R) and EP-SG (15% SG, H) resins were studied. Fig. 6 shows the kinematic viscosity as a function of time for 7 weeks at 50°C . The viscosities

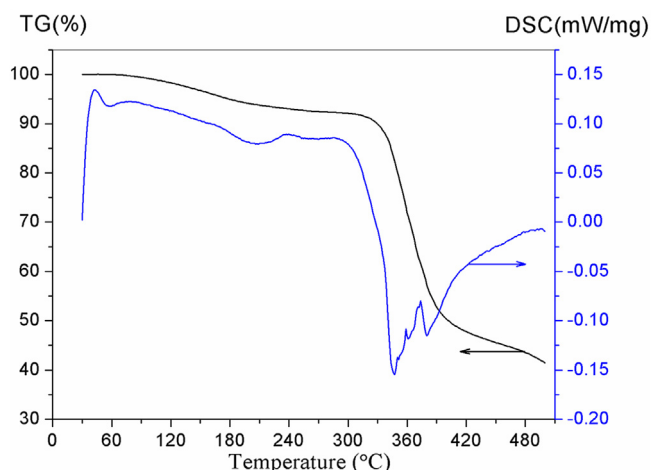


Fig. 7. TG-DTA curves from the EP-SG (15% SG, H) resin.

of EP-SG (15% SG, R) and EP-SG (15% SG, H) increase with time. However, both materials maintain their flowability after 7 weeks of storage at 50 °C. Compared to EP-SG (15% SG, R), EP-SG (15% SG, H) has a lower viscosity and exhibits less change in viscosity. For EP-SG (15% SG, H), it is thought that some of the hydroxyl and epoxy groups in EP react with the isopropoxy group in SG and that the unreacted chelate bonds are stable. However, with EP-SG (15% SG, R), some isopropoxy groups remain in the system after reaction at room temperature, and can react further at 50 °C. Therefore, EP-SG (15% SG, H) is more stable and can be stored at room temperature for one year.

As an anticorrosive coating matrix for heat exchangers, this resin should offer good thermal, physical, and chemical properties. Because of its good storage stability, EP-SG (15% SG, H) was chosen for characterization of the properties listed above.

3.3. Thermal properties

It is necessary to study curing behavior to obtain coatings with excellent properties. DSC is a convenient tool for examination of the curing behavior of resins. Fig. 7 shows the TG-DTA curves of the EP-SG (15% SG, H) resin. A broad exothermic peak appears in the DSC curve at about 172 °C, and may be regarded as the onset of curing of the EP-SG (15% SG, H) resin. In the TG curve, little weight loss occurs below 80 °C. The losses decrease slowly due to volatilization of solvents as the temperature increases. When the temperature reaches at 172 °C, the EP-SG (15% SG, H) resin starts to cure. During the curing process, water and some small molecules are generated and volatilized, leading to further weight loss. The EP-SG coating maintains a constant weight in the temperature range of 240 °C–330 °C. However, its weight decreases rapidly as it decomposes above 300 °C. The thermal degradation of the cured EP-SG (15% SG, H) resin is shown in Fig. 8. The thermal degradation temperature is defined as the temperature at which the samples lose 5% of their initial weight. It can be seen that 5 wt% loss occurs at 335 °C. In summary, the thermal degradation temperature is 335 °C, which indicates that the coatings exhibit good thermal resistance.

3.4. Physical properties

The physical properties of the cured EP-SG (15% SG, H) coating are shown in Table 2. The cured EP-SG (15% SG, H) coating possesses excellent adhesion, flexibility, and impact resistance, which meet the requirements for anticorrosive coatings to be used with heat exchangers.

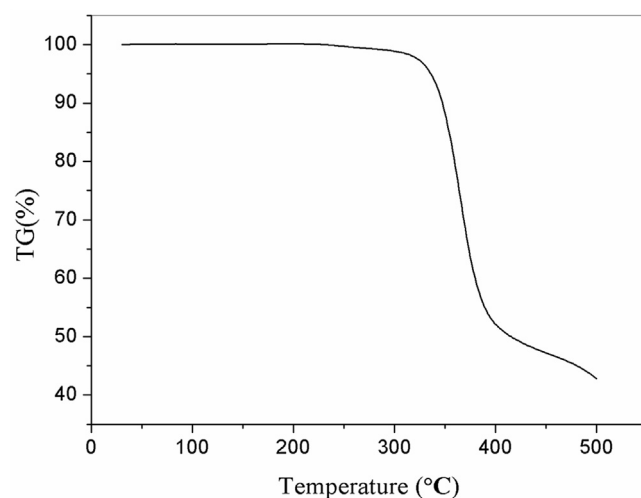


Fig. 8. TG curves for the cured EP-SG (15% SG, H) resin.

Table 2

Mechanical properties of the cured EP-SG (15% SG, H) coating.

Experiment	Results
Adhesion force, grade	1
Flexibility, mm	≤1
Impact resistance, cm	≥50

Table 3

Chemical resistance of the cured EP-SG (15% SG, H) coating.

	Cracking spots	Blisters	Color change
Boiling water	None	None	None
Boiling seawater	None	None	None
10 wt% NaOH solution	None	None	None
5 wt% HCl solution	None	None	None
5 wt% H ₂ SO ₄ solution	None	None	None
Xylene	None	None	None
Toluene	None	None	None
Acetone	None	None	None
Diesel	None	None	None
Gasoline	None	None	None

3.5. Chemical resistance

Chemical resistance tests were carried out to determine the ability of the EP-SG coatings to withstand specific conditions (Table 3). First, water resistance was measured in pure, boiling water and boiling seawater. After two weeks, no changes to the coatings were found. Examination of the chemical resistance was performed by immersing the coatings in various solvents such as a 10 wt% sodium hydroxide (NaOH) solution, 5 wt% hydrochloric acid (HCl) solution, 5 wt% sulfuric acid (H₂SO₄) solution, xylene, toluene, acetone, diesel, and gasoline. After six months of immersion, there were no signs of cracking spots, blisters, color change, or other indications of solvent attack observed with any of the films. These results indicate that the cured EP-SG (15% SG, H) coating possesses fairly good chemical resistance.

4. Conclusions

A self-curing, thermosetting EP-SG resin was synthesized via a reaction between the isopropoxy group of SG and the hydroxy or epoxy groups of EP. The EP-SG resin has stable performance at room temperature and can be self-cured via heating. The curing mechanism includes the breaking of chelate bonds at high temperatures and formation of new reactive groups. The resulting reactive groups

can react further with those hydroxy or epoxy groups from EP that did not react during the synthesis process. The EP-SG resin synthesized at 80 °C with 15% SG has good storage stability and can be stored for more than one year without gelation. In addition, cured EP-SG coatings exhibit good thermal and chemical resistance, as well as good physical properties. They can be used as the binder of a new anticorrosive paint for heat exchangers.

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