



Self-curing poly (2, 6-dimethyl-1, 4-phenylene oxide)-organic titanium chelate resin for thin anticorrosive coatings



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ABSTRACT

Poly (2, 6-dimethyl-1, 4-phenylene oxide) (PPO) has been extensively investigated as an outstanding engineering plastic. Functionalized PPO with low molecular weight has been widely studied to expand its applications, while there are relatively few reports on PPO-containing coatings. In this work, a terminal phenolic hydroxyl group PPO (RPPO) with low molecular weight was synthesized by redistribution of high molecular weight commercial PPO with bisphenol A via benzoyl peroxide as an initiator. The self-curing, thermosetting RPPO-organic titanium chelate resins were first developed via the reaction between phenolic hydroxyl groups in RPPO and isopropoxy groups of diisopropoxy titanium bis (acetylacetonate). Thin coatings with 10 μm thickness could be obtained by heat curing without any curing agents. Characterization using Fourier transform infrared spectroscopy and ^{13}C nuclear magnetic resonance showed evidence of the successful preparation of the self-curing, thermosetting resins. The curing behavior and thermal stability were assessed via differential scanning calorimetry and thermogravimetric analysis. The mechanical properties of the cured coating were discussed and the chemical resistance was tested using accelerated immersion tests. Benefited by the self-curing mechanism, issues of non-uniformity, bubbles, and low storage stability caused by curing agents were avoided. It was found that the thin coating possessed good thermal and mechanical properties. Owing to the rigid aromatic chain structure and strong Ti-O bond in the crosslinked structure, the glass transition temperature was improved and the thermal degradation temperature could reach up to 402 $^{\circ}\text{C}$. No degradation was found after 72 h accelerated immersion tests in boiling water, boiling seawater and boiling butanone, which should be critical to the resin's potential application for anticorrosive coating.

1. Introduction

Poly (2, 6-dimethyl-1, 4-phenylene oxide) (PPO) and its derivatives have been outstanding engineering plastics for more than 50 years [1–4]. Attributed to its low dielectric constant, PPO is one of the materials with the potential to satisfy the demand for copper clad laminate, especially for use as the basic material in high-frequency printed circuit boards [5–7]. Commercial physically modified PPO has been widely adopted ascribed to its high glass transition temperature (approximately 212 $^{\circ}\text{C}$), low water absorption, low flammability and high dimensional stability [8,9]. In addition, PPO has been used to improve the fracture toughness of thermosetting networks, which extends its performance in the automobile and machinery industries [10,11].

However, high molecular weight thermoplastic PPO possesses high melt viscosity and poor film-forming ability, which limits its processing and final application. Moreover, the low resistance to non-polar solvents and non-curable nature also discount its use [2,3]. Therefore, control of the molecular weight of PPO is an important issue for

modifying their properties. It is noteworthy that different from the traditional physical modification, low molecular weight PPO with functionalized groups can be obtained by chemical modification.

The redistribution of high molecular weight commercial PPO to increase reactive functional groups in per chain is an elegant chemical modification method [12–15]. Well-studied by White and others, many redistribution processes for producing low molecular weight PPO with phenolic, epoxide or vinyl-terminated groups have been developed [12,15]. In addition, low molecular weight PPO can also be prepared by the oxidative polymerization of 2, 6-dimethyl phenol in the presence of a copper-amine-complex catalyst under oxygen. By introducing bromo, vinyl, and epoxide groups into PPO sequentially, a new class of thermosetting polymers with PPO as the backbone were synthesized [16–22]. Interestingly, attributed to the absence of polar groups in the polymer backbone, PPO possesses excellent separation properties that make them suitable candidates for gas separation [18,19]. Through further reactions such as quaternization and functionalization with hindered fluorene side chains, PPO can be employed to prepare proton

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and anion exchange membranes [20–22]. However, to the best of our knowledge, no PPO-containing coating for anticorrosion protection has been reported.

Titanium chelates are formed from tetraalkyl titanates or halides and bi- or polydentate ligands. They are known to react easily with active groups to form complexes with significantly different properties from the starting materials [23–26]. Titanates are often used in epoxy-based paint, because they can promote hardening of epoxy resins and improve adhesion of metals to epoxies [23,24]. The phenolic compounds can react with the organic titanate to form a highly colored titanium phenolate and can be crosslinked by heating. The acetylacetonate complexes of titanium function as adhesion promoters for the ink binder while also improving the cold-storage stability of the products [23,25]. Due to titanium's high affinity for oxygen atoms, titanium chelates can bond to oxide surfaces, to yield a scratch-resistant oxide coating [26].

Recently, single-component, self-curing coatings have gained attention because of their long pot life, reducing the probability of coating defects, convenience, and ability to cure without an agent [27–29]. For example, novel self-curable cathodically depositable coatings were developed from glycidyl functional epoxy ester-acrylic graft co-polymer without using any external crosslinking agents [27]. In our previous work, a self-curing, thermosetting resin (EP-SG resin) based on epoxy and organic titanium chelate were prepared as an anticorrosive coating matrix for heat exchangers [29]. Benefited by the self-curing mechanism, the resin has good storage stability and can be stored for more than one year without gelation.

Given the diversity and wide usage of PPO in blending modification, high-frequency printed circuit boards and exchange membranes, there are few studies about PPO-containing anti-corrosion coatings. The goal of our present work is to fill that gap. In this research, a self-curing PPO-organic titanium chelate resin with a long pot life, was synthesized using redistributed PPO (RPPO) and diisopropoxy titanium bis (acetylacetonate) (GBA). Without the addition of a curing agent or catalyst, thin coatings with potential for use in corrosion prevention can be obtained by thermal crosslinking. The reaction mechanism of the PPO-GBA resin was investigated via Fourier transform infrared spectroscopy, ^{13}C nuclear magnetic resonance. The curing behavior and thermal stability were assessed via differential scanning calorimetry and thermo-gravimetric analysis. Moreover, the mechanical properties as well as the effect of the RPPO and GBA on chemical resistance performance were investigated.

2. Experimental methods

2.1. Materials

PPO ($M_n = 28500$, polydispersity index (PDI) = 2.5) was supplied by Nantong Xingchen Synthetic Material. Co. Ltd, Ruicheng Branch. Bisphenol A (BPA) and benzoyl peroxide (BPO) were purchased from J & K Scientific, China, and used as received. Diisopropoxy titanium bis (acetylacetonate) ($\text{Ti}(\text{CH}_3\text{COCHCOCH}_3)_2(\text{C}_3\text{H}_7\text{O})_2$) solution (75 wt.% in isopropanol) was purchased from the E.I. Du Pont Company, USA. Tinplate sheets and carbon steel bars were purchased from Dongguan Dalai Instrument Co., Ltd. Toluene, xylene, tetrahydrofuran (THF) and methanol were obtained from Tianjin Heowns Biochem Technologies LLC, Tianjin, China. All other reagents were supplied by Tianjin Kernel Reagent Co., Ltd, China, and used without further purification.

2.2. Synthesis of redistributed PPO (RPPO)

The redistributed PPO (RPPO) was prepared according to the literature method [12,13]. Briefly, PPO (20 g, 0.7 mmol) and BPA (1.84 g, 7 mmol) were dissolved in 100 mL toluene at 90 °C under argon atmosphere. Subsequently, BPO (0.58 g, 2.1 mmol) was added dropwise over 1 h. After maintaining the reaction at 90 °C under an argon

atmosphere for another 6 h, the mixture was allowed to cool to room temperature and then added to methanol to precipitate the product. The resulting product was collected by filtration and then dried in a vacuum oven at 80 °C. The dried product was ground to powder, washed with methanol several times, and finally obtained.

2.3. Preparation of the RPPO-GBA resin

RPPO-GBA resin was prepared by weighing the desired ratio of RPPO and GBA (20 wt.% GBA with respect to RPPO) into a glass jar. Then, the blend ingredients were dispersed in xylene (4:1 w/w solvent/blends) using an ultrasonic vibrator (100 W, 40 kHz) for 30 min. Finally, the obtained resins were sealed for further use.

2.4. Preparation of the RPPO-GBA coating

The tinplate sheets with dimensions of 120 mm × 35 mm × 0.2 mm were used as substrates for the physical and mechanical tests. The sheets were prepared using sandpaper with grit sizes of 800, rinsed thoroughly with acetone and ethanol, and then air-dried prior to use. For the immersion tests, carbon steel bars with 100 mm long and 10 mm in diameter were also treated similarly. According to the GB/T1727-1992 standard, the above RPPO-GBA resin solution was dip-coated onto the treated iron sheets or carbon steel bars, then dried at room temperature for 1 h. All coated samples were cured at 200 °C for 2 h in an air-circulating oven. Attributed to the low solution concentration (20 wt.%), the dry film thickness of all samples was measured to be $10 \pm 2 \mu\text{m}$. The thickness of the coating was measured by means of an electromagnetic thickness gauge according to ISO 2808.

2.5. Characterization

The relative molar mass and PDI of the prepared RPPO were determined using gel permeation chromatography (GPC, Waters 1515–2414). The flow rate was 1 mL/min of THF at 40 °C. The structure analyses of the RPPO-GBA resins upon curing were conducted using Attenuated Total Reflectance FTIR (ATR-FTIR) and ^{13}C solid-state nuclear magnetic resonance (NMR) spectra. ATR-FTIR spectra were recorded using a spectrum 100 FTIR spectrometer (FTS3000, BIORAD, USA) in the range from 4000 cm^{-1} to 400 cm^{-1} . The RPPO-GBA coating was cured at 200 °C for 2 h and then used as the IR sample. The solid-state ^{13}C NMR spectra were recorded on a JNM-ECA400 (JEOL Co. Ltd., 100 MHz). The RPPO-GBA resins and cured coatings were pulverized and put into zirconium sample tubes. The ^{13}C NMR spectra were characterized with the CP/MAS method.

In order to determine the reaction process, research the thermal stability of the coating and find an ideal curing temperature, the curing behavior and thermal stability of RPPO-GBA resin was assessed with differential scanning calorimetry (DSC) and thermo gravimetry analysis (TGA). TGA was performed with a simultaneous thermal analysis (DSC/DTA-TG, NETZSCH, STA 409 PC Luxx[®], Germany) under a nitrogen atmosphere at a heating rate of 10 °C/min from 30 °C to 500 °C. DSC was performed with a diamond differential scanning calorimeter (NETZSCH DSC 200 F3, Germany) under a N_2 atmosphere. The samples were first heated at 10 °C/min from 50 °C to 280 °C and held for 5 min, and then cooled to 50 °C at 10 °C/min. They were maintained at 50 °C for 5 min and then heated to 280 °C at 10 °C/min again. The glass transition temperature (T_g) of each cured sample was determined by the second heating scan.

The pencil hardness of the RPPO-GBA coatings was determined using standard pencils according to ASTM D3363-74. Flexibility was tested using the QTX-Paint Film Flexibility Tester (Dongguan Dalai Instrument Co., Ltd) according to GB/T 1731–1993 standard. The flexibility is presented by the smallest diameter of mandrel bar in which cracking was not observed. Impact strength was measured by an impact testing machine (Tianjin Weida Testing Machine Manufacturer) with a

load of 1 kg from a given height of 50 cm according to the GB/T1732-93 standard. The adhesive force was measured using circle-cut tester (Tianjin Zhonghuan Reagent Instrument Works) under the GB/T1720-1979 standard. A sharp steel needle was used to draw circles on the surface of samples. Then examine the integrity of the scratch marks to evaluate the firmness of the adhesive on the substrate. This standard ranks the adherence in 7 grades, grade 1 being the coatings with the strongest adherence.

Coated carbon steel bars were placed in pure boiling water and boiling seawater at atmospheric pressure for 72 h for water resistance tests. The samples were also immersed in boiling butanone for 72 h. Besides, 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, xylene and gasoline, and allowed to sit for 120 days at room temperature. After immersion, a visual examination was performed to detect deterioration such as blistering, cracking or spoiling.

3. Results and discussion

A lot of work has been done in developing PPO-containing materials, and commercial organic titanium compounds are already widely used. In order to explore a facile way to produce feasible self-curing, thermosetting resin, RPPO and organic titanium chelate were adopted. After thermal curing, thin anti-corrosion coatings were formed. The whole strategy to fabricate the self-curing resin and coating is illustrated in Fig. 1.

3.1. Synthesis of RPPO, RPPO-GBA resin and RPPO-GBA coating

The RPPO fabrication method is illustrated in Fig. 2. According to the results of the GPC analysis, as shown in Fig. 3, the molecular weight

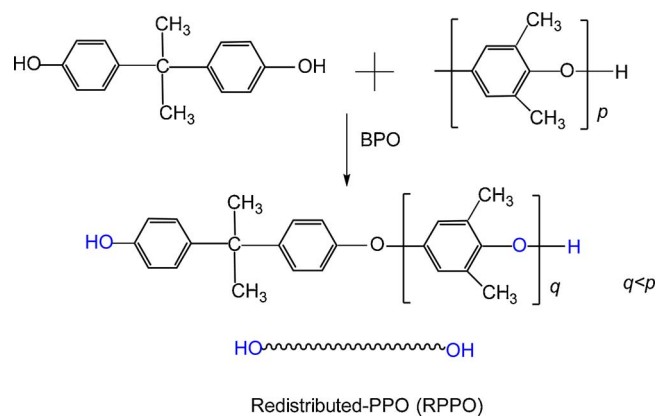


Fig. 2. Synthesis of RPPO.

of the RPPO decreased from $M_n = 28000$ to $M_n = 8000$, accompanied by a decrease of the PDI from 2.2 to 1.9, suggesting that low molecular weight RPPO was obtained successfully.

Representative ATR-FTIR spectra of RPPO, RPPO-GBA resin and RPPO-GBA cured coating are given in Fig. 4. As shown in Fig. 4(a), the peak at 3650 cm^{-1} is attributed to the stretching vibrations of $-\text{OH}$ groups. The peaks noticed at 1610 cm^{-1} and 1180 cm^{-1} corresponding to $\text{C}=\text{C}$ stretching of aromatic ring and $-\text{C}-\text{O}-\text{C}-$ stretching, respectively, which confirm the formation of RPPO. Thus, the bisphenols were predominantly incorporated at the PPO chain and the carbon of the PPO repeating unit, which is consistent with the GPC results. For the RPPO-GBA resin sample in Fig. 4(b), the characteristic peak at 1530 cm^{-1} is assignable to the $-\text{C}-\text{O}$ stretching of $\text{CH}_3\text{COCHCOCH}_3$

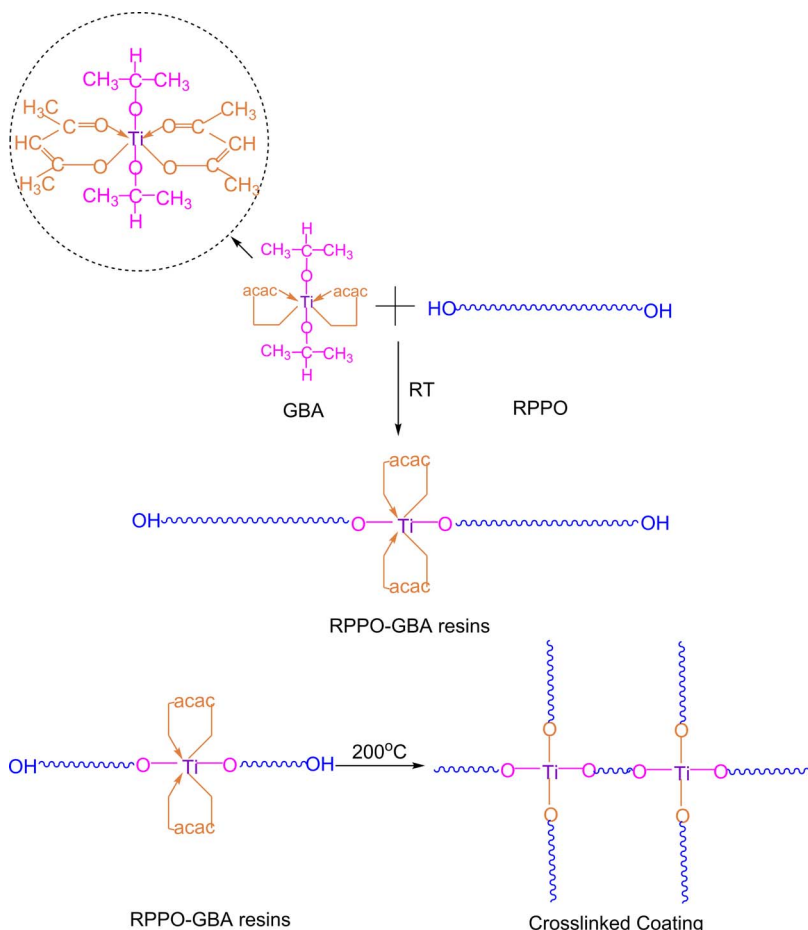


Fig. 1. Schematic illustration of the formation of RPPO-GBA resin and RPPO-GBA coating.

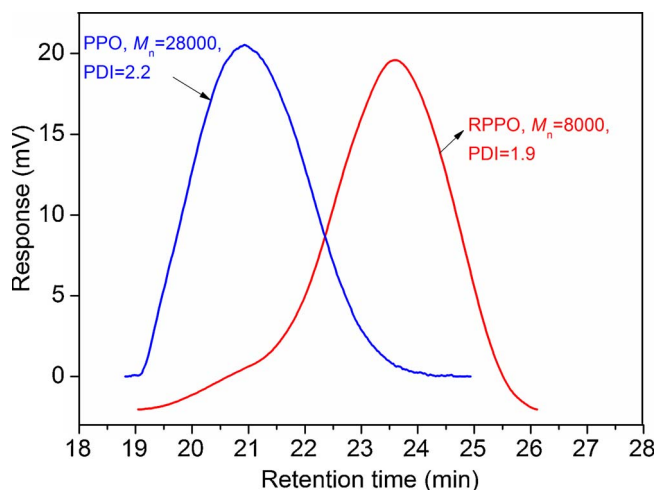


Fig. 3. GPC spectra of PPO and RPPO.

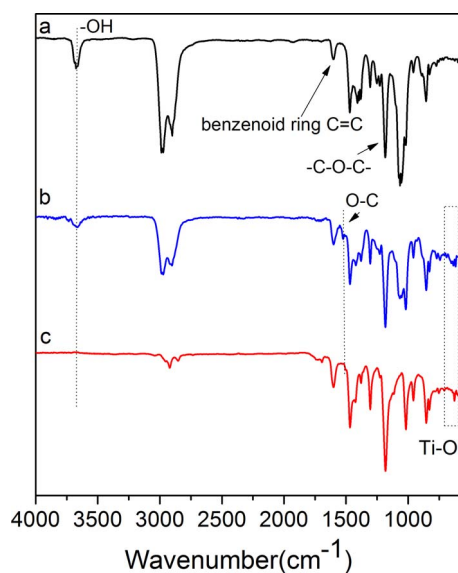


Fig. 4. ATR-FTIR spectra of RPPO (a), RPPO-GBA resin (b) and RPPO-GBA coating (c).

groups, which are in accordance with those in the GBA sample [30,31]. The weakening of the peak at 3650 cm^{-1} indicates that the $-\text{OH}$ groups have reacted with isopropoxy groups to generate the resins. As shown in Fig. 4(c), for the RPPO-GBA cured coating, the disappearance of characteristic peaks at 3650 cm^{-1} and 1530 cm^{-1} demonstrates the complete reaction between $-\text{OH}$ groups and acetylacetonate groups. The retained absorptions at 600 cm^{-1} assignable to Ti-O stretching of phenoxy-titanium structures, indicate the formation of a crosslinked network.

As shown in Fig. 5(a), the ^{13}C NMR spectrum of RPPO has three peaks at 165, 126 and 110 ppm, which were assigned to the carbon atoms on the benzene ring in RPPO. The sharp peaks at 21.8 ppm in each sample were assigned to the $-\text{CH}_3$ groups. For RPPO-GBA resin (Fig. 5(b)), with GBA added, a sharp peak near 190 ppm assignable to $\text{CH}_3\text{COCHCOCH}_3$ of the ketone group from acetylacetonate was found. Peaks at 77 ppm and 60 ppm corresponding to $\text{CH}_3\text{COCHCOCH}_3$ of methine and methyl, respectively, were also found [31]. In the RPPO-GBA coating sample (Fig. 5(c)), the disappearance of the peaks at 190 ppm, 60 ppm and 77 ppm, indicates that acetylacetonate groups have reacted with hydroxyl groups to generate the crosslinked structure, which was in line with the ATR-FTIR results.

Hence, it was observed from the ATR-FTIR and ^{13}C NMR spectra that two chemical steps were involved in the formation of RPPO-GBA

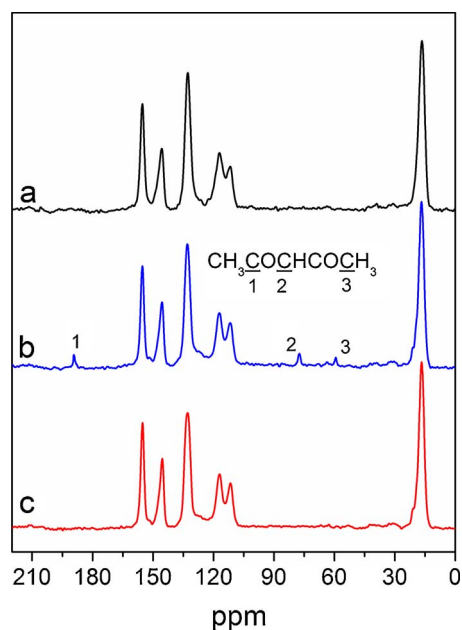


Fig. 5. ^{13}C NMR spectra of RPPO (a), RPPO-GBA resin (b) and RPPO-GBA coating (c).

resins and the formation of the RPPO-GBA coating, which are shown in Fig. 1. Isopropoxy groups are known to be much more rapidly attacked by hydroxyl groups [32]. Thus, the first step is the alcoholysis reaction. Bifunctional hydroxyl groups react readily with isopropoxy groups in GBA to obtain highly colored RPPO-GBA resin at room temperature. The generated RPPO-GBA resins have a good pot life and can be stored for more than one year without gelation ascribed to the better cold-storage stability of GBA and the dynamic balance of the alcoholysis reaction between RPPO and GBA [30]. On the other hand, the resultant resins dissolved in a solvents containing isopropanol. The isopropanol could prevent further reaction between hydroxyl groups and isopropoxy groups, improving the cold-storage stability of the product. In the second step, the breaking chelate bonds can participate in a direct condensation reaction at $200\text{ }^\circ\text{C}$, generating a highly crosslinked RPPO-GBA structure with a Ti-O bridge. Therefore, through heat curing, a self-curing RPPO-GBA coating could be obtained without the addition of any curing agents.

3.2. Thermal behaviors of the RPPO-GBA resin and RPPO-GBA coating

Fig. 6 represents the thermal degradation of RPPO-GBA resins and RPPO-GBA coating. The thermal degradation temperature at 5 wt.% loss (T_d) and char yield at $500\text{ }^\circ\text{C}$ for all samples are summarized in Table 1. Attributed to the regular aromatic chain structure, PPO has high decomposition temperature [33]. The T_d of RPPO in our study reached $380\text{ }^\circ\text{C}$. In Fig. 6(a), for the RPPO-GBA resins, a broad exothermic peak in the DSC curve and the initial thermal degradation T_d at $190\text{ }^\circ\text{C}$ are due to the reaction between the hydroxyl groups and isopropoxy groups as well as the reaction between chelating acetylacetonate groups and hydroxyl groups. The second stage of degradation above $400\text{ }^\circ\text{C}$ is due to the degradation of the aromatic structure. For the RPPO-GBA coating (Fig. 6(b)), no exothermic peak or thermal degradation were found below $400\text{ }^\circ\text{C}$, indicating that the coating was crosslinked completely. Owing to the well-defined aromatic chain structure and strong Ti-O bond in the crosslinked structure, T_d could reach up to $402\text{ }^\circ\text{C}$.

The glass transition temperature (T_g) of each sample was determined by the second heating scan. In representative DSC curves (Fig. 7), no peaks for melting transitions were observed, suggesting that these PPO polymers are amorphous. Compared with commercial high molecular weight thermoplastic PPO ($T_g \approx 212\text{ }^\circ\text{C}$), the values of T_g for

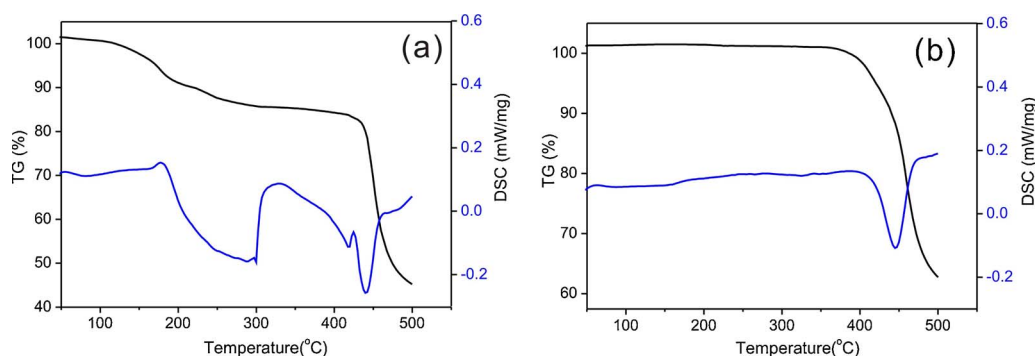


Fig. 6. TGA curves of RPPO-GBA resin (a) and RPPO-GBA coating (b).

Table 1
DSC and TGA results of RPPO, RPPO-GBA resin and RPPO-GBA coating.

Sample	T_g (°C)	T_d (°C)	Char yield at 500 °C (100%)
RPPO	200	380	44%
RPPO-GBA resins	–	190	45%
RPPO-GBA coating	205	402	63%

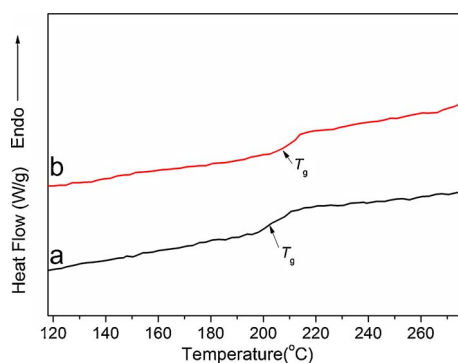


Fig. 7. DSC curves of RPPO (a) and RPPO-GBA coating (b).

RPPO were slightly lower, at 200 °C, owing to the shortening of the aromatic chain. Compared with the RPPO sample, the T_g of RPPO-GBA coatings increased to 205 °C, due to the presence of the Ti-O cross-linking structure. In summary, for RPPO-GBA coatings, T_d and T_g could reach up to 402 °C and 205 °C, respectively, which indicates that the coatings exhibit good thermal resistance.

3.3. Physical and mechanical properties of RPPO-GBA coating

To perform its duty effectively, the physical and mechanical properties of RPPO-GBA cured coating are shown in Table 2. For comparison, the properties of EP-SG coating [29], which is discussed in our previous work and has been commercially produced, are also shown. No traces of cracks were observed, indicating that RPPO-GBA coatings have excellent impact resistance. Also, the pencil hardness test carried out for the coating indicates that it can resist scratching up to a hardness of 2H, which we ascribe to the rigid aromatic chain structure and the presence of sufficient titanium chelates for crosslinking. It is

Table 2
Physical and mechanical properties of RPPO-GBA coating and EP-SG coating.

Samples	RPPO-GBA coating	EP-SG coating
Film Thickness	10 ± 2 μm	180 ± 5 μm
Pencil hardness	2H	2H
Flexibility, mm	≤ 1	≤ 1
Adhesion force, grade	1	1
Impact resistance, cm	≥ 50	≥ 50

presumed that good performance is dependent upon good adhesion [34]. The adhesion of RPPO-GBA coatings can reach to 1 grade with integrated morphology at the edges or within the circles. The excellent adhesion of the coatings could be attributed to the presence of chelated titanates, which shows very good adhesion to metal surface [24,34]. The flexibility test for the coated panel carried out at the mandrel diameter of 1 mm showed no appearance of cracks. The high flexibility of the coating is also attributed to its good adhesion to the substrate. As shown in Table 2, compared to commercially produced EP-SG coating, the cured RPPO-GBA coating in our study also possesses excellent adhesion, flexibility, and impact resistance, and thus meets the requirements for anticorrosive coatings.

3.4. Water and chemical resistance properties of RPPO-GBA coating

Immersion tests are used to determine the ability of a coating to withstand specific conditions [29,35]. The chemical and water resistance properties of the RPPO-GBA coating are reported in Table 3 and photographs of coated carbon steel bars after immersion tests are shown in Fig. S1. The accelerated immersion test was carried out in both boiled pure water and seawater to emulate the aggressiveness of different environments. As shown in Fig. S1, after 72 h of exposure, no blisters, water penetration, color changes or cracking spots were found on RPPO-GBA coatings, indicating excellent resistance performance in water and seawater environments.

Examinations of the chemical resistance were also performed by immersing the coatings in various chemical solvents including boiling butanone, xylene, acetone, gasoline, 5 wt.% HCl solution, and 10 wt.% NaOH solution. Similarly, after an accelerated immersion test for 72 h in boiling butanone or 120 days of immersion in the above solvents, no signs of any degeneration were observed on RPPO-GBA coatings.

An important aspect in relation to applications in elevated temperatures is to ensure that the temperature does not exceed T_g of the coating, because this will result in degeneration [36]. In our work, it is worth noting that the high T_g of RPPO-GBA coating could result in a higher resistance to erosion at elevated temperatures. Moreover, the hydrophobic nature of RPPO and a fully crosslinked hard coating

Table 3
Water and chemical resistance of RPPO-GBA coating and EP-SG coating.

	Samples	RPPO-GBA coating	EP-SG coating
Water resistance	Boiling water	None ^a	None
	Boiling seawater	None	None
Chemical resistance	Boiling butanone	None	None
	Xylene	None	None
	Gasoline	None	None
	HCl solution (5 wt.%)	None	None
	NaOH solution (10 wt.%)	None	None

^a The word “None” represents no blisters, color changes or cracking spots generated.

provides good barrier properties to water and corrosive chemical species.

Anticorrosive protection does not depend only on the nature of the coating used to protect a metallic surface, even associated with the thickness factor. As a comparison, the chemical and water resistance properties of commercially produced EP-SG coating are also presented in Table 3. Noticeably, as compared to EP-SG coating with thickness of 180 μm , RPPO-GBA coating with good water and chemical resistance is on the order of 10 μm in thickness, which would simplify the construction process and reduce costs. These findings are of great importance in the design of new types of anticorrosive coating.

4. Conclusions

The terminal phenolic hydroxyl group, RPPO, with a low molecular weight was synthesized by redistribution of high molecular weight commercial PPO, then blended with GBA to prepare a self-curing resin by a reaction between the isopropoxy groups of GBA and the hydroxyl groups of RPPO at room temperature. The generated RPPO-GBA resin has a long pot life at room temperature, capable of being stored for more than one year without gelation, and can be self-cured via heating. At high temperatures, the breaking chelate bonds can participate in a direct reaction with hydroxyl groups, leading to the formation of a crosslinked network.

The thin coating with 10 μm -thickness not only exhibits good mechanical properties, such as hardness, adhesion, impact strength and flexibility, but also shows good thermal stability up to 402 $^{\circ}\text{C}$. No degradation was found after 72 h of accelerated immersion tests in boiling water, boiling seawater and boiling butanone, indicating good water and chemical resistance of RPPO-GBA coating. Thus, the self-curing RPPO-GBA resin can be a good candidate for anti-corrosion protection.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.porgcoat.2017.10.010>.

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