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Synthesis and characterization of hyperbranched polyether/DGEBA hybrid coatings

Xuepei Miao[a,b,∗∗], An Xing[a,b], Weiduo Yang[a,b], Lifan He[b], Yan Meng[b,∗], Xiaoyu Li[a,∗]

[a] State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China
[b] Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, PR China

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ABSTRACT

The design and synthesis of high performance epoxy anti-corrosion coatings are very desirable; however, they still remain a big challenge until today. In this paper, epoxide-terminated hyperbranched polyether (EHBPE) was incorporated into epoxy coatings to enhance the corrosion resistance. EHBPE/DGEBA hybrid coatings were characterized by rheometer, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), low-field nuclear magnetic resonance (NMR) crosslink density spectrometer, and contact angle meter. Effects of EHBPE loading on the corrosion resistance of hybrid coatings were investigated. Results show that hybrid coating containing 5% EHBPE shows considerable enhancement in corrosion resistances compared with the neat DGEBA coating, which can be explained by the higher crosslink density, less structural defects, and possible fewer free volume. Results suggest that the EHBPE/DGEBA hybrid coating has much improved corrosion resistance and can be used an anti-corrosion coating.

1. Introduction

Metal corrosion is a serious waste of resources worldwide. In order to save energy and money, various research works, including addition of corrosion inhibitor, cathodic protection, and surface coatings, have been used to reduce the corrosion damage. Anti-corrosion coating is widely used because of its low cost and ease of application. For the same reason, among the different types of coatings, organic coating is most commonly used [1–3]. Epoxy coatings have dominated the anti-corrosion coating industry because they have excellent adhesion properties, low-shrinkage, good corrosion resistance and chemical resistance [4]. However, their wider application is limited due to the intrinsic brittleness. In addition, when high corrosion resistance is required, typical epoxy formulation is not completely satisfactory. Thus, lots of efforts have been made to further improve the corrosion resistance of epoxy coating. Several materials such as thermoplastics, [5] siloxane modifiers, [6] and liquid rubber, [7] have been used to modify the epoxy coating either by chemical or physical methods. Blending thermoplastics into epoxy leads to notable increases in the total viscosity, which is undesirable for processing. When siloxane and liquid rubber are added, reaction-induced phase separation can occur, which is sensitive to processing and thus compromises the flexibility in cure scheme and processing conditions. Thus, to improve the corrosion resistance of coatings, new and effective technologies are needed.

It is worth of noting that pinholes in the coating are always the fatal shortcoming of epoxy coatings. Electrolyte solution may react with metal at the interface through the pinholes, and resulting corrosion. A dense film will improve the corrosion resistance of coatings. In general, the higher the crosslink density, the denser the coating. Therefore, increase the crosslink density will enhance the corrosion resistance. In addition, rheological properties of polymers are closely related to the processability of coatings. Low viscosity of polymers can improve processability. In recent years, hyperbranched polymers (HBPs) with highly branched structure have shown great potential as a modifier due to its lower viscosity and more functional groups, [8,9] and several research works have reported the enhancement of crosslink density of neat DGEBA systems using HBPs as modifier [10–15]. Recently, a hybrid organo-silicate corrosion resistant coatings using hyperbranched poly (ethylene imine) as cross-linking agent have been reported [16]. Results show that films containing PEI, demonstrate better corrosion protection properties compared to formulations containing corrosion inhibitors and employing DETA as a cross-linking agent. Allauddin [17] reported organic–inorganic hybrid coatings using epoxy terminated hyperbranched polyester (EPHBP) and curing agents such as APTMS and HMMA. The cured films show higher elongation at break due to the use of HMMA and presence of unmodified epoxide groups. Ganjaee Sari

∗ Corresponding authors.
∗∗ Corresponding author at: State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China
E-mail addresses: miaoxp@mail.buct.edu.cn (X. Miao), mengyan@mail.buct.edu.cn (Y. Meng), lixy@mail.buct.edu.cn (X. Li).

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[18] studied the epoxy/clay nanocomposites using clay particles modified with polyester-amide hyperbranched polymer. Results revealed that surface modification of the clay particles by HBP caused significant enhancement of the epoxy coating corrosion resistance especially when the 'polymer/clay' ratios were 10/1 and 5/1. Ikladious [19] synthesized alkyd resins based on the glycolyzed PET waste and hyperbranched polyesters with different vegetable oil fatty acids and studied their potential applications in coating areas. All films exhibited good adhesion, bending, impact and ductility. Among the reported HBPs, commercially available Boltorn® series hyperbranched molecules with polyester backbones, are most widely used [20]. However, polyester structure is known for poor chemical resistance to bases. Hyperbranched molecules with polyether backbones are more chemically stable and appear to be more promising than hyperbranched polyesters [11,12,15]. To the best of our knowledge, no work has focused on using hyperbranched polyether as modifier for anti-corrosion epoxy coating.

In this work, we present the preparation of hybrid epoxy coating by incorporating EHBPE into DGEBA and cured with amine. Properties of amine-cured hybrid epoxy coatings were characterized by rheometer, EIS, SEM, low field NMR, and contact angle meter. Results indicate that incorporating appropriate amounts of EHBPE does not increase the viscosity and can effectively enhance corrosion resistance of epoxy coatings. Explanations and possible mechanisms for the improved corrosion resistance are also provided.

2. Experimental

2.1. Chemicals

Diglycidyl ether of bisphenol A (DGEBA) was purchased from Yueyang Resin Factory, China (EEW = 190.04 g/equiv.). LITE3000 was purchased from Cardolite Co. Ltd. (China). Xylene, butanone, and terahydrofuran (THF) were purchased from Beijing reagent Co., China. m-dihydroxybenzene and tetrabutylammonium bromide (TBAB) were purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). 1,1,1-Trihydroxymethylpropane triglycidyl ether (TMPGE) (99%) was purchased from Titanchem Co. Ltd. (Shanghai, China). $CDCl_3$ were purchased from Beijing InnoChem Science & Technology Co. The metal matrix was Q235 mild steel panels (100 mm × 50 mm × 1 mm). The steel panels were polished using 400# abrasive paper to remove mill scale. Then the steels panels were cleaned with acetone and ethanol successively. All solvents and reagents are analytical pure and were used as received.

2.2. Preparation of EHBPE

Fig. 1 shows the chemical structure of EHBPE. EHBPE was synthesized by proton transfer polymerization [21,22]. Detailed information about preparation of EHBPE is provided in supporting information (SI). The chemical structure of EHBPE was confirmed by nuclear magnetic resonance (^{1}H NMR) spectroscopy and Fourier transforms infrared spectroscopy (FTIR) as shown in SI.

2.3. Preparation of hybrid coatings

As illustrated in Fig. 2, predetermined amounts (i.e., 3%, 5%, 10%, 15%, and 30% by total weights of epoxy) of EHBPE and DGEBA were mixed by mechanical mixing at 60 °C for 2 h. After cooling to 25 °C, mixed solvent of xylene and butanone with a ratio of 7:3 (v:v) were added into the mixture under continuously stirring. Then, 120% (molar ratio) LITE3000, curing agent, were added into the mixture under continuously stirring until the mixture became uniform and transparent. Next, hybrid coatings were applied on cold rolled mild steel panels and silicone rubber by spray coating. Subsequently, the coated panels were cured at room temperature for a week. Finally, edge seal was performed on hybrid coatings, which were coated on mild steel panels, using paraffin. The coating thickness is about 60 ± 5 μm.

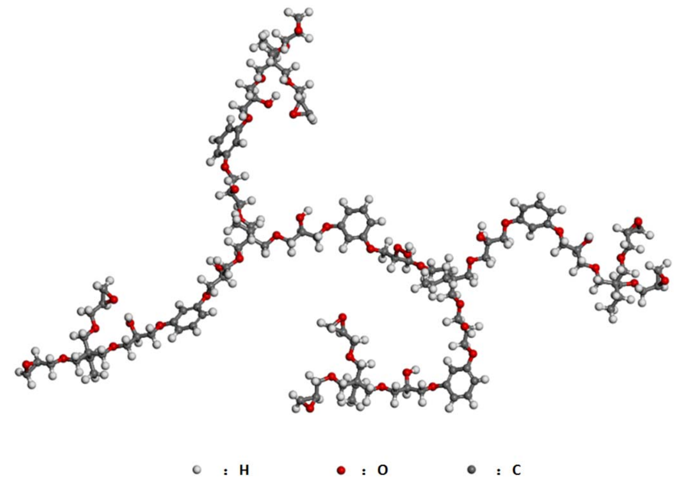

Fig. 1. The chemical structure of EHBPE.

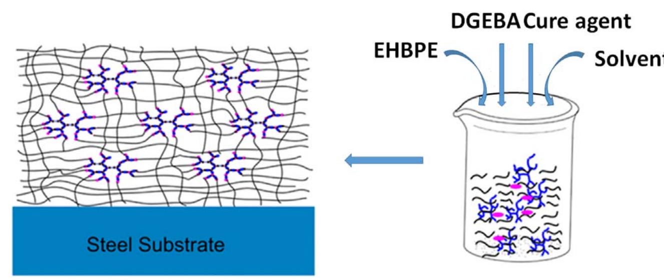

Fig. 2. Preparation of hybrid coatings.

2.4. Corrosion testing

In order to accelerate the failure process of the coatings, 10% H_2SO_4 solution and deionized water were chosen to perform the corrosion test. The coated samples were immersed in 10% H_2SO_4 solution and deionized water, 7 cm depth to the solution surface. The maximum immersion time was up to 140 days. Coatings that coated on silicone rubber were used to perform water absorption tests. Surface area of specimens obtained from silicon rubber is 1 cm × 1 cm. Every day the specimens were removed from the corrosion environment (deionized water) and dried used filter paper, then the specimens were weighed and recorded. Water absorption was calculated according to the following equation:

$$MC = \frac{m_i - m_0}{m_0} \times 100\%$$

where MC is the water absorption, m_i, the weight after immersion tests, m_0, the weight before immersion test.

2.5. Characterization

Rheological measurements were performed on an MCR301 rheometer (Anton Paar, Austria) with 25 mm cone-plates. The temperature accuracy is controlled within 0.1 °C using a peltier temperature-controlled device. In order to avoid transient effects, pre-shearing is used before measurements. The rheological measurements were carried out at ambient temperature (~25 °C).

Electrochemical Impedance Spectroscopy (EIS) was conducted on an ZAHNER electrochemical workstation using a three electrode system with a frequency range of 100 KHz to 0.1 Hz. The coated panel has an exposed area of approximately 10 cm^2, which served as the working electrode, saturated calomel electrode (SCE) as reference electrode, and