



## Effect of curing agent molecular structures on the tribological and corrosion behaviors of epoxy resin coatings



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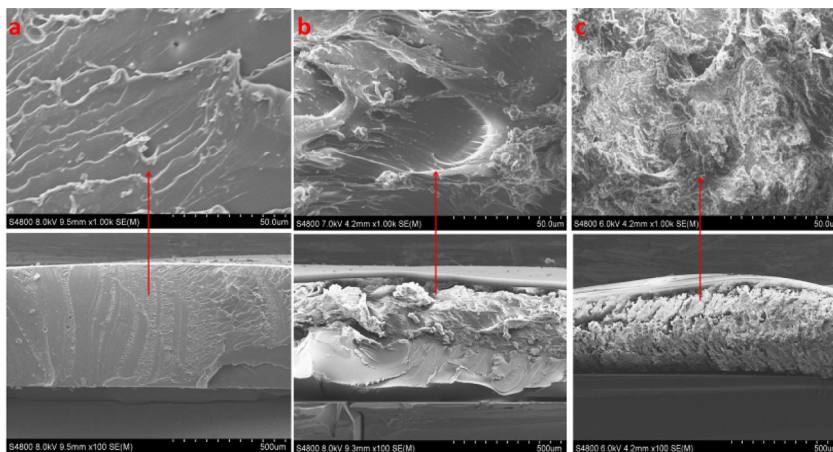
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### HIGHLIGHTS

- Three curing agents with different molecular structures were used to cure epoxy resins (EP).
- The effect of molecular structures on the tribological and anti-corrosion properties of EP was evaluated.
- The tribological and anti-corrosion mechanisms of EP coatings were analyzed.

### GRAPHICAL ABSTRACT

Fracture surfaces morphologies of EP coatings cured by three kinds of curing agents with different molecular structures. (a) DETA cured; (b) IPDA cured and (c) *m*-PDA cured.



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### ABSTRACT

In order to study the influence of curing agent molecular structure on the tribological and corrosion behaviors of epoxy resin (EP) coatings, EP coatings were cured by three kinds of curing agents with different molecular structures including diethylenetriamine (DETA), isophorone diamine (IPDA) and *m*-phenylenediamine (*m*-PDA). The curing degree of EP coatings was identified by fourier transform infrared spectrometer (FTIR). The element composition and chemical bond structure of the as-prepared coatings were tested by X-ray photoelectron spectrometer (XPS). The tribological properties of the as-prepared coatings were assessed by UMT-3 multi-functional tribology test equipment and surface profiler. The anti-corrosion behaviors of the coatings were evaluated by an electrochemistry workstation in 3.5 wt% NaCl. The internal structure and wear trace morphologies of the coatings were observed by scanning electron microscopy (SEM). Using of curing agents with different molecular structures resulted in different tribological and anti-corrosion properties for EP coating. While the coefficient of friction (COF) of

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EP coating cured by *m*-PDA was the highest, the one cured by DETA was the lowest, which may be due to the linear and flexible chain offered less resistance during the sliding process and hence it displayed the lowest COF. Besides, the anti-corrosion performance of EP coating cured by IPDA was the best and the one cured by *m*-PDA was the poorest, which may be attributed to molecular structure and molecular weight which can influence the crosslink network and interface structure of EP coatings significantly. At last, the tribological and anti-corrosion mechanisms of EP coatings with different molecular structures were discussed in detail.

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## 1. Introduction

Ocean, which covers 71% of the earth's surface, contains abundant resources. With the shortage of resource, ocean development will constantly grow and more and more metal and alloys will be demanded, and a large part of the international trade in the world today is transported by cargo boat in sea [1,2]. As marine environment containing a vast array of caustic substance, metal and alloys will be damaged due to the penetration of  $\text{Cl}^-$  ion in seawater. Statistically, the loss of American economy by corrosion reached 276 billion dollars in 1998, which accounted for 3.1% of US Gross National Product [3–5]. Besides, the pumps, open hydraulic drive system and blades etc. are also damaged during their operating condition in marine environment. According to some statistics, Chinese Gross Domestic Product of ocean was 3.1964 trillion and the loss caused by friction and wear in the ocean was approximately 143.9 billion in 2009 [6,7]. Therefore, study and improvement the tribological performance and anti-corrosion ability of materials which used in marine environment are imperative.

So far, fabrication of organic coating on the surface is a cost-effective way to protect metal and alloys [8]. Epoxy resin (EP) is one of most widely used thermosetting resins for organic coatings with excellent anti-corrosion, mechanical strength, and dielectric properties. However, its application is limited due to high brittleness, poor wear resistance, low moist heat resistance and peeling strength, etc. [9,10]. Therefore, it is necessary to improve its tribological performance and anticorrosion ability by modifying EP. Zhang et al. [11] prepared a new curing agent based on palmitoleic acid methyl ester modified amine (PAMEA) along with diethylenetriamine (DETA) and EP was cured by it with different contents. The results showed that the PAMEA curing agent can improve the impact strength, modulus and strength of cured EP in comparison with DETA curing agent. The crosslinking density of cured EP is maximal when PAMEA/EP weight ratio is 30/100. Boey et al. [12] investigated the effect of different curing agents such as (4,4'-diaminodiphenylsulfone (DDS), 4,4'-diaminodiphenylmethane (DDM) and meta-phenylene diamine (*m*-PDA)) in microwave curing of an EP system on the final cured glass-transition temperature ( $T_g$ ). The results indicated that DDM and *m*-PDA systems with different electron-donating functional groups were able to achieve maximum cure degree and  $T_g$  values equaled to those thermally cured at significantly shorter curing time. Ji et al. [13] investigated EP modified with various silane monomers under the catalysis of organotin compound and characterized the corrosion resistance by electrochemical impedance spectroscopy (EIS). The results indicated that corrosion performance of EP coatings was obviously improved after the chemical modification with silane monomers, which can be attributed to the reduction of water absorption and formation of a chemical Si–O–Me interfacial layer.

Organic coatings can form the “shielding” structure, and most of them are polymers whose structures are certain to influence significantly the tribological properties and anti-corrosion properties of organic coatings [14]. Kondo [15] investigated that tribological and anti-corrosion properties of the newly synthesized perfluoropolyether (PFPE) whose terminal group is an ammonium salt

with a carboxylic acid comparing to the conventional PFPEs. The results showed that with the increased length of amine molecule chain, the frictional coefficient decreased and anti-corrosion ability increased due to the modified PFPE uniformly covering the magnetic surfaces. Ahn et al. [16] investigated the tribological behavior of self-assembled monolayers (SAMs) with  $\omega$ -functional *n*-alkanethiol compounds at nanoscale using a friction force microscopy (FFM) and at the microscale using a microtribometer. The results indicated that the kinetic friction coefficient of the SAMs decreased as  $\text{COOH} \gg \text{OH} > \text{CH}_3$  and the longer hydrocarbon chain SAMs with the same functional group showed a slightly higher friction coefficient at the nanoscale because of the stronger lateral cohesion among hydrocarbon chains. Perry et al. [17] investigated the tribological properties of poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG)-coated oxide interfaces and found that interfacial friction reduced with the increase of PEG side-chain length and the decrease of molar ratio of L-lysine monomer to PEG side chain.

From the above, it can be concluded that curing agents with different molecular structures could contribute to the crosslinking and interface structure of as-prepared coating, which must have a great influence on the chemical and physical properties of coating. In this work, three curing agents with different molecular structures, including the chain-shaped of diethylenetriamine (DETA), ring with side-chain shaped of isophorone diamine (IPDA) and benzene-shaped of *m*-phenylenediamine (*m*-PDA) were used to cure EP. Then cured EP coatings were obtained on the cast irons surface and the effect of curing agents with different molecular structures on the tribological and anti-corrosion properties of EP coatings were investigated systematically.

## 2. Experimental

### 2.1. Materials

The matrix EP E-20-75 was purchased from NBHT NEW MATERIALS Co., Ltd., China. The curing agent DETA, solvent including *n*-butyl alcohol and xylene were purchased from Sinopharm Chemical Reagent Co., Ltd., China. The curing agent IPDA and *m*-PDA were purchased from Aladdin Industrial Corporation Co., Ltd., China. The molecular structures of curing agents used in this work are shown in Fig. 1.

### 2.2. Determination of epoxy value

The curing degree of epoxy resin is determined by epoxy value. While the curing agent content was insufficient would cause not fully curing, an excess of curing agent content will reduce the properties of cured EP. So the epoxy value of the EP, which was 0.258, was measured in accordance with the previous literatures.

### 2.3. Preparation of the epoxy coatings

The E-20-75 with a weight of 3 g was diluted and stirred in the mixed solvent containing (the mass ratio of *n*-butyl alcohol and

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