



Toughening mechanisms of rubber modified thin film epoxy resins: Part 2—Study of abrasion, thermal and corrosion resistance



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ABSTRACT

This paper presents corrosion and abrasion resistance of an epoxy system modified by using a synthesized epoxy terminated polybutadiene (ETPB) resin with good toughening properties. The effect of this modification on the hardness, abrasion, thermal and corrosion protection performance of the resultant modified coatings was investigated. Pendulum hardness test showed that the incorporation of ETPB into epoxy matrix increased damping energy of the system. Taber experiment showed that rubber modification increased abrasion resistance of epoxy coatings. Thermal gravimetric analysis (TGA) of samples showed that the thermal resistance of ETPB modified epoxy coatings was almost the same as that for the neat one. The corrosion protection performance of rubber modified and unmodified epoxy coatings were investigated using electrochemical impedance spectroscopy (EIS) in 3.5% sodium chloride solution for a period of 90 days. EIS studies showed that both coatings remained intact with good corrosion resistance properties. Film resistance of unmodified and ETPB modified epoxy coatings after 90 days of immersion were found to be $2.59 \times 10^{10} \Omega \text{ cm}^2$ and $2.70 \times 10^{10} \Omega \text{ cm}^2$, respectively. The addition of hydrophobic butadiene rubber into epoxy resin increased the water contact angle from 77° to 85° . This increment in hydrophobicity decreased the water uptake of modified epoxy coating.

1. Introduction

Metallic substrates are commonly protected by organic coatings against environmental attacks such as corrosion, abrasion and chemicals. The effectiveness of these coatings depends on many factors such as barrier performance and permeability against corroding ions, mechanical properties, adhesion to substrate and their integrity [1,2]. Among organic coatings, epoxy resins are used for a wide variety of protective coatings due to their very good properties such as low shrinkage, ease of cure, high temperature performance, stiffness, chemical and corrosion resistance and good adhesion to many substrates [3,4]. Usually, epoxy coatings are compared to polyurethane coatings which are more ductile and more resistant against impact and abrasion, but epoxy has showed better corrosion and higher stiffness. However, one major drawback of cured epoxy coatings is their relatively poor impact and crack propagation resistance [5]. This is due to the three-dimensional molecular structure of cross linked epoxy resins which reduces their rotational and translational freedom and also the chances for primary bonds to be set up with adjacent molecules [6].

As mentioned above, epoxy coatings have good performance as

protective coatings. However, low ductility is a serious challenge to use epoxy as protective coatings. Furthermore, their barrier action can fail due to the formation of cracks on the coating films which is related to their poor impact resistance. By crack propagation, more surface area of substrate is exposed to corrosive environment and the aqueous environment penetrates easily through the crack and reaches to metallic substrates. Consequently, a corroding system is driven by this defect in which cathodic and anodic reactions take place spontaneously at the interface of metal and corrosive environment. Thus, the poor resistance of the epoxy coatings to crack propagation is one of the parameters which leads to intensify the corrosion of substrate. Also, high hardness causes weak abrasion resistance which has restricted the use of epoxy coatings for applications where the coating is exposed to abrasion. Therefore, many researchers have worked on the toughness modification of epoxy coatings.

The modification of epoxy coatings by reactive liquid rubbers is one of the most common and widely used methods to enhance the toughening of epoxy coatings [7–12]. In conventional procedure, epoxy resin and liquid rubber are generally mixed or pre-reacted and a homogeneous solution is prepared. Rubber particles precipitate as a second

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phase after curing of this homogeneous solution [13,14]. In fact, as epoxy coating cures the configurational entropy of system decreases due to increase in molecular weight and phase separation occurs [15]. It was found that employing of a small amount of liquid reactive rubber can cause dramatic improvements in impact resistance of epoxy resins [7–12]. The precipitated rubber particles act as stress concentrators. They could dissipate energy through the main toughening mechanisms in rubber modified epoxy systems which are rubber cavitation and induced shear deformation in the matrix. In addition, several secondary toughening mechanisms such as plastic void growth [11–14] rubber particle bridging [16,17], crack deflection, crack bifurcation and crack pinning may also contribute to the elevated toughness of modified epoxies [10].

Hydroxyl terminated polybutadiene (HTPB) is one of the liquid rubbers which has been used to improve the toughness of epoxy resin [18,19]. The main drawback of HTPB is its poor compatibility with epoxy resins [20]. High interfacial interaction between rubbery phase and epoxy is an important factor for improvement of toughening and impact resistance of epoxy coatings. To enhance HTPB and epoxy resin compatibility and to impart an effective interfacial adhesion, both constituents should be chemically joined together. The low reactivity of HTPB toward epoxide groups necessitates the chemical modification of HTPB through the use of a bi-functional reagent that would react with both groups. Silane coupling agent [21] and toluene-2,4-diisocyanate (TDI) [22] are generally used to improve the compatibility of the second rubbery phase with epoxy resin. In our previous work [23], HTPB was reacted with maleic anhydride and the produced carboxyl group reacted with an epoxy and an epoxidized HTPB was prepared. Then the epoxidized HTPB (ETPB) was added into an epoxy resin at 5, 7.5 and 10 wt.%. The results showed that the sample containing 7.5 wt.% of rubber had provided the highest fracture toughness, improving fracture toughness and fracture energy of neat epoxy from $0.65 \text{ MPa m}^{1/2}$ and 84 J/m^2 to $1.80 \text{ MPa m}^{1/2}$ and 793 J/m^2 , respectively. Moreover, in that paper different mechanisms of toughening in bulk and film were studied, but other important properties of protective coatings were not determined. Therefore, in this research the hardness, abrasion resistance, thermal resistance and corrosion resistance of ETPB modified epoxy coatings were evaluated.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol-A (DGEBA) with an epoxy equivalent weight (EEW) of 190 g/equiv which was supplied by Huntsman Co. was used. The epoxy resin was cured by a cycloaliphatic amine as curing agent (Epikure F-205 from Huntsman Co.). The number of amine groups of hardener was reported to be 104 g/equiv . Hydroxyl terminated polybutadiene (HTPB) was provided by Zibo Qilong Chemical Industry Co. Ltd. Maleic anhydride (M.A) and triphenylphosphine (T.P.P) were purchased from Merck. All chemicals were used as received.

2.2. Synthesis and characterization of epoxy terminated polybutadiene

The detail of synthesis procedure of epoxy terminated polybutadiene from hydroxyl terminated polybutadiene was reported in our previous work [23]. Briefly, Synthesis of epoxy terminated polybutadiene was carried out in two steps. In the first step, carboxyl terminated polybutadiene (CTPB) was synthesized by reacting 22.84 gr HTPB with 5.06 gr maleic anhydride through a ring opening addition reaction at $80 \text{ }^\circ\text{C}$. This reaction was performed in the presence of 100 gr epoxy resin to control the viscosity build up during the reaction. The reaction was carried out in a three necked 250 milliliter glass reactor which was equipped with a mechanical stirrer and was blanketed with nitrogen. The reaction time was 24 h to ensure complete reaction of reagents. In the next step, ETPB was synthesized by reacting the

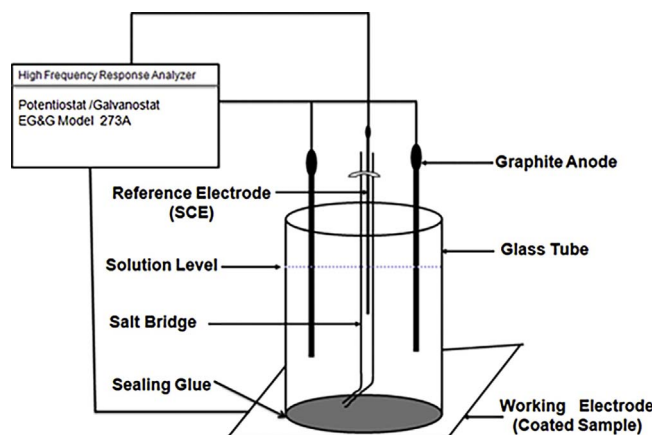


Fig. 1. Schematic of electrochemical cell.

Table 1
Abrasion index and hardness of neat epoxy and ETPB modified epoxy.

Sample	AI(± 0.0005)	Pendulum hardness (number of oscillation)	Vickers hardness (HV)
Neat Epoxy	0.0299	135 (± 2)	23.2(± 1.1)
7.5 wt.%ETPB modified	0.0114	129(± 1)	20.6(± 0.8)

resulted CTPB with an addition of 72.24 gr epoxy resin (i.e. 7.5 wt.%) in the presence of 0.2 wt.% of triphenylphosphine as catalyst. The reaction was performed at $80 \text{ }^\circ\text{C}$ and under vacuum (12 mmHg) for 24 h.

2.3. Samples preparation

In order to evaluate the effect of ETPB on the behavior of ETPB modified epoxy coatings, the neat epoxy resin and the synthesized ETPB were first degassed for 1 h at 5 mbar in a vacuum oven. In our previous work [23] it was found that the sample containing 7.5 wt.% of ETPB presented the best fracture resistance. Therefore, 7.5 wt.% of synthesized ETPB was chosen and the required amount of curing agent (103.16 gr) was added into the mixture and then was mixed under vacuum for 30 min at 1300 rpm. A neat epoxy sample was considered as the reference. A graduated film applicator (BYK-Gardner, Germany) was used to apply coatings on ST12 mild steel sheets from Mobarake steel Company (Iran) test panels. Curing process was performed in an air circulating oven at $80 \text{ }^\circ\text{C}$ for 3 h, followed by 1 h of post curing at $120 \text{ }^\circ\text{C}$. A layer thickness gauge (i.e. QuaNix 1500) was used to measure coating thickness. The measurements were carried out on five different positions on plates and the average thickness of each sample was found to be about $250 \pm 20 \mu\text{m}$.

2.4. Abrasion resistance and hardness measurements

A pendulum hardness tester (Elcometer 3034, UK) was used to measure pendulum hardness of coatings according to ASTM D 4366. A Leica VMHTMOT hardness tester with a Vickers indenter was used to measure micro-hardness of coatings. Normal force of 98.1 mN was loaded during 12 s to measure the micro-hardness. These measurements were carried out on three replicate specimens and at three different points on each replicate.

Abrasion resistances of epoxy and ETPB modified epoxy films were evaluated using a standardized Taber abrasion tester according to ASTM D 4060. CS10F wheels with 250 g loads on each wheel were utilized. Abrasion cycles were chosen to be 800. The abrasion index (AI) was then recorded using Eq. (1):

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