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New detailed insights on the role of a novel praseodymium nanofilm on the polymer/steel interfacial adhesion bonds in dry and wet conditions: An integrated molecular dynamics simulation and experimental study

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ABSTRACT

The adhesion improvement and surface-bonding nature at epoxy polymer/steel interface decorated with novel rare earth element nanofilms based on praseodymium (Pr) and its composite cerium-praseodymium (Ce-Pr) oxides were studied by molecular dynamics (MD) simulation and experimental approaches. The steel surface morphology and chemistry after depositing praseodymium and cerium oxides were examined by field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The adhesion characteristics of epoxy coating applied over surface-treated steel were assessed by pull-off adhesion and Fourier transform infrared (FT-IR) spectroscopy. Results revealed that the adhesion strength at polymer/steel interface substantially improved upon steel surface treatment by Pr and Ce-Pr (100%) nanofilms. The strongest interfacial adhesion and the lowest adhesion loss in wet conditions were observed for steel samples decorated by Ce and Pr oxides. The simulation results further evidenced the stronger epoxy resin adhesion onto surface-treated steel (represented by praseodymia Pr_2O_3 and ceria CeO_2) as compared with untreated sample (represented by iron oxides) particularly under wet conditions.

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1. Introduction

The metal surface includes very thin oxide layers that can be created during exposure to oxygen. These oxide films play an important role in the creation of weak adhesion forces at the polymer/metal interface. The hydroxyl (-OH) functionalities can be created on the steel surface covered with metal oxides through oxides hydration [1–4]. The hydrated oxide surfaces enhance the wetting of metal by polar polymers. Epoxy is a popular thermosetting polymer with widespread applications in different industries thanks to its good chemical properties, high mechanical strength, proper thermal stability, and good adhesion to most of the metals [5,6].

However, the existence of hydrated oxide layer on the metal surface leads to the adsorption of polar and non-polar organic contaminations on the metallic substrate. The presence of such weak layers at the polymer/metal interface brings about the ap-

pearance of weak adhesion bonds. In fact, the contaminations reduce the access of the polymeric polar groups and the adhesion sites on the metal surface [7,8]. One approach to overcome this difficulty and to obtain strong adhesion bonds between a polymer and a metal surface is pre-treatment of metal prior to application of polymeric coating. It has been proven that polymer/metal interface with strong adhesion bonds can be achieved through removal of the weakly bonded oxide layers, organic contaminations and roughening the surface [9,10]. Besides the surface free energy and wettability characteristics, the number of active adhesion sites available for bonding with polar groups of polymer can be increased by this way [9–13].

It is possible to create strong electromagnetic bonding (hydrogen bonding) between polar moieties (i.e., epoxide and hydroxyl) of epoxy polymer and hydrated metal oxides exist on the metal surface. Additionally, roughening the metallic surface increases its real surface area and provides some cavities and pores on the surface. The polymer chains penetrate into these cavities and pores and thereby make some physical bonds [14,15]. Another adhesion mechanism involving in polymer-metal bonding is the dispersion (i.e., van der Waals) forces [16]. All of these provide good epoxy

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adhesion onto metal under dry situations. However, the polymer-metal adhesion bonds are not strong enough to resist against water molecules in wet environments. Once water molecules reach the interface the loss of adhesion occurs. As it has been previously discussed, the main adhesion mechanism of epoxy coating over the metallic substrate is the hydrogen bonding interactions formed between the epoxy polar groups and the metal oxides exist on the surface. Despite the good barrier properties of epoxy polymers against water diffusion, the water transport to the interface of polymer/metal occurs via diffusion into the pores, cavities and defects existed in the polymer matrix [17,18]. Water molecules at the interface could readily deteriorate the epoxy-metal hydrogen bonds as they are strong hydrogen bonding agents. It has been reported that emergence of a weak water layer at the polymer/metal interface gives rise to coating delamination [19–22]. The hydration of the oxide layer located at the coating/metal interface also weakens the adhesion bonds. In the presence of water molecules the electrochemical reactions initiate underneath the coating, and hydroxyl ions are formed as a result of cathodic reaction. These anions interact with Na^+ cations and form NaOH species which is a strong alkaline agent, leading to the increase of pH beneath the coating. The alkaline condition intensifies the adhesion bonds destruction and coating delamination [23–25].

There are numerous methods for the enrichment of the durability of interfacial adhesion bonds under wet conditions. The use of chemical coupling agents and formation of stable metal oxides are two examples of these methods. One effective strategy for obtaining strengthened polymer-metal adhesion bonds with high durability in wet conditions is the chemical treatment of metal surface by stable oxidized films. The engineering of the chemistry and physics of the polymer/metal interface can result in the creation of strong bonding between polymer and metal surface. It has been demonstrated that hydrogen bonds are not stable in wet conditions and there is a need for attaining strong chemical bonds. In our previous efforts, the beneficial role of metal surface treatment by chromates [26,27], zirconium [28,29] and phosphate [30–32] on the polymer/steel interfacial adhesion bonds improvement in dry and wet conditions were reported. Also, in our recent studies the chemical treatment methods based on rare earth compounds have been considered [33–36]. The chemical treatment by rare earth compounds like cerium gives stable oxide films on the metal surface with improved polymer/metal interfacial adhesion bonds. Compared to the conventional chemical treatment techniques like chromating and phosphating, the chemical treatment methods based on rare earth materials are environmentally friendly [32,33]. It has been shown in our prior investigations that the incorporating cerium oxide film at the polymer/metal interface significantly enhances the interfacial bonds. Also, strong chemical adhesion bonds with high durability against water molecules can be obtained applying this approach. It has been shown that the cerium oxide film can increase the surface free energy, work of adhesion and surface roughness. The wettability of metal surface by polymer can be significantly improved by deposition of cerium oxides [33–36]. The film of cerium oxide, which is stable in wet condition, restricts the cathodic reaction and reduces the coating displacement from the substrate.

In the present study, in the first part it was intended to develop a novel chemical treatment based on rare earth element praseodymium and its composite with cerium to enhance the strength and durability of epoxy coating/steel interfacial adhesion under both dry and wet conditions. In the second part, the interfacial adhesion of epoxy resin organic coating onto bare and surface-treated steel substrates was studied from computational views. Computational investigations using MD simulations were carried out in both dry and wet environments. Besides MD simulations, the electronic-structure properties of epoxy resin respon-

sible for its adsorption behavior were assessed via ab initio quantum mechanics (QM) methods applying density functional theory (DFT).

2. Experimental and computational methods

2.1. Raw materials and sample preparation

In the current study, the steel panels (0.04 wt% Al, 0.05 wt% P, 0.05 wt% S, 0.19 wt% C, 0.32 wt% Mn, 0.34 wt% Si, and 99.01 wt% Fe) with dimension of 5 cm × 7 cm × 0.2 cm were prepared from Foolad Mobarakeh Co. (Iran). All reagents required for preparation of Ce and Ce-Pr chemical solutions, including praseodymium nitrates, $\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, hydrogen peroxide, H_2O_2 , cerium nitrate, $\text{Ce}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, NaOH and HCl (37%), were purchased from Merck Co. (Germany). Also, the epoxy resin, Araldite GZ 7071X 75, and polyamide hardener, CRAYAMID 115, were prepared from Saman (Iran) and Arkema Co., respectively. Prior to Ce and Ce-Pr film deposition over the sample the steel substrates were abraded by 600, 800 and 1000 grits SiC papers, cleaned with acetone solvent, washed with deionized water and finally dried.

2.2. Chemical treatment of steel sheets by PrONP and Ce-PrONP

The Pr chemical treatment bath was prepared by adding 1 g/L $\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 1 g/L H_2O_2 , and 8 mL/L HCl 37%. The Ce-Pr bath was prepared through adding 1 g/L $\text{Ce}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 1 g/L $\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 1 g/L H_2O_2 , and 8 mL/L HCl 37%. The pre-cleaned steel samples were dipped in the Pr and Ce-Pr containing baths for 5 min, temperature of 45 °C and pH of 3. All samples were washed with deionized water after chemical treatment and dried in an oven at 120 °C for 2 h. Finally, the epoxy/polyamide (1.3:1 w/w) coating was applied on the steel samples with and without chemical treatments, dried at room temperature for 24 h and cured in an oven at 100 °C for 1 h. The dry film thickness of the cured epoxy films was $80 \pm 5 \mu\text{m}$.

2.3. Characterization

SEM/EDS, Phenom ProX, Phenom-World B.V., Eindhoven, AFM, Dualscope DS 95–200, DME, X-ray photoelectron spectroscopy, Specs EA 10 Plus, with Al $K\alpha$ radiation at a pressure of 109 mbar, and OCA 15 Plus-type system were employed for the characterization of the morphology, microstructure and surface chemistry of the steel samples modified by PrONP and Pr-CeONP. A Posi test-pull off adhesion tester (DEFELSKO) was employed for the characterization of adhesion strength of the epoxy-coated samples. A FT-IR diffuse reflectance spectroscopy (Model Bruker IFS66 with an MCT detector), a resolution of 4/cm and an acquisition of 100 scans, was used for studying the nature of bonds between the epoxy and steel surface.

2.4. Quantum mechanics optimization of epoxy resin

Before MD simulations, the first-principles quantum mechanics (QM) approaches were applied to fully optimize the geometry of epoxy resin coating molecule. Fig. 1 demonstrates the molecular structure of diglycidyl ether of bisphenol A (DGEBA) type epoxy resin. This epoxy resin was utilized as an organic adsorbate for exploring its adhesion onto both untreated and surface-treated carbon steel substrates. The QM methods based on density functional theory (DFT) techniques were used to get electronic/atomic details concerning the electronic features of epoxy resin coating molecule influencing its binding to metallic substrates.

To this purpose, the potential energy of DGEBA epoxy resin was sequentially minimized to find its lowest energy geometry. First,

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