



On the enhanced corrosion resistance of elastomer-modified polybenzoxazine/graphene oxide nanocomposite coatings

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ABSTRACT

In this study, we demonstrate the use of rubber-modified polybenzoxazine (PBZ)/graphene oxide (GO) as a coating to protect carbon steel from corrosion. GO, acting as the nanofiller, is added in increasing amounts to enhance the barrier property of the resulting nanocomposite coatings. Results via immersion in chloride solution coupled with standard electrochemical measurements show that the rubber-modified PBZ is able to protect carbon steel from corrosion attack. Even more, the coatings containing small amounts of GO provided enhanced protective abilities for the carbon steel. By varying the amount of GO, the protective property is tuned and the optimum GO concentration that could offer the most enhanced corrosion resistance property is determined.

1. Introduction

One of the standard and proven applications against corrosion is the use of coatings that contain inorganic inclusions such as chromates, phosphates, and oxides [1]. However, due to the health effects that they pose [2], researchers are now gearing towards the utilization of polymer-modified materials as corrosion protective coatings. Polymer modification is a method of developing novel and/or tailor-made polymeric materials by altering the physical and/or chemical structure of existing polymers [3]. It involves the use of macro-, micro-, and nano-sized solid as impermeable fillers and reinforcements to improve the behavior and performance of a polymer customized for a specific application. The reinforcement and the fillers not only improve the mechanical property (e.g. stiffness and toughness), but also enhance the barrier property of the polymer making it applicable as an effective barrier against corrosive environments [4]. Some of these are glass fiber- [5], carbon fiber- [6], and carbon nanotube- [7] reinforced polymeric materials for corrosion-resistant equipment. Two-dimensional fillers (flakes, platelets, and ribbons) made of glass, mica, and layered silicates are also used to improve the barrier property of the polymeric materials making them suitable as coating and lining for corrosion protection and barrier applications [8].

Polymer modification can also be accessed by combining two or more polymers in the form of polymer blends and copolymers such that

the best properties of each component are achieved in a single functional material. This combination of properties is expected to improve processability, mechanical properties, chemical and heat resistance, etc. As a result, these types of materials find applications in numerous fields such as adhesion, coatings, and design of composite materials [9]. A good example of polymer blend is poly(vinylidene fluoride)/poly(methyl methacrylate) which is used in coating automotive parts to impart light stability and gasoline resistance [10]. Copolymers, such as acrylonitrile-butadiene-styrene (ABS) and styrene-butadiene rubber (SBR) [10–12], which provide better toughness, have also been utilized.

In our study, we report a facile way of fabricating a nanocomposite coating composed of polybenzoxazine (PBZ), rubber, and graphene oxide (GO) for corrosion protection of carbon steels from chloride attack. Carbon steel is used, as it is the most widely studied and used engineering materials especially in the field of corrosion [13,14]. Thermosetting PBZ possesses properties such as near-zero shrinkage upon polymerization [15,16], low surface free energy [15–18], dielectric [15,16,19,20], thermal, and mechanical properties [15,16]. In addition, PBZ has low water absorption [15,16], making it a good polymer candidate for our coating study, as surface hydrophobicity plays a very significant role in corrosion resistant function of coatings [21,22]. Moreover, to our knowledge, there are only few reports on PBZ associated with corrosion-resistance coatings [23–26].

Until now, even with the several properties previously emphasized,

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PBZ still suffer from brittleness [27,28] which limits their application. Consequently, a good number of literatures on PBZ have focused on overcoming the brittleness of the cured materials [27]. Several approaches have been designed to toughen thermosetting materials; and one of the most promising is the modification with rubber. It has been found that rubber modification is a very effective approach to overcome the inherent brittleness of thermosets [29,30]. For instance, physical blends of PBZ and rubber have improved fracture toughness [31,32] without undue sacrifices to the desirable properties [33]. Hence, in our study, PBZ is toughened by blending the synthesized benzoxazine (BZ) with hydroxyl-terminated and epoxidized polybutadiene (HTBD) rubber via melt mixing [29]. HTBD is selected as the toughening modifier as the epoxidized rubber can undergo copolymerization with the hydroxyl groups formed upon opening of the BZ ring and thus can be chemically grafted into the matrix network [16].

To further improve the barrier performance and enhance the corrosion resistance, we added GO as the nanofiller. To date, there has been no study involving the application of rubber-modified PBZ/GO nanocomposite as protective coating. Previous studies have shown that when coated onto metal surfaces, GO is an effective protection coating [34] and a proven barrier to the diffusion of oxygen; thus, it is able to render protection from environmental oxidation [35–37]. Also, GO-containing composite materials display better barrier properties against oxygen gas and water compared with neat polymeric materials [38]. To test for the potential application in corrosive environments, the resulting PBZ/rubber/GO-coated (PRG), PBZ/rubber-coated (PR), and uncoated steel substrates were immersed in 0.5 M NaCl solution, and the corrosion resistance was evaluated by standard electrochemical measurements, and results were compared.

2. Experimental

2.1. Materials

Impact-resistant carbon steel sheets (Type A516) were obtained from McMaster Carr and was used as the substrates. The steel sheets had thickness of 1.59 mm and composition of 0.10% C, 1.00% Mn, 0.60% Si, 0.035% P, 0.035% S, and Fe making up the remaining percentage by mass. Pro grade advanced silicon carbide papers, used in polishing the substrates, were purchased from 3M.

Phenol (99% purity) and potassium permanganate (KMnO_4) crystals were purchased from EMD Chemicals Inc., while graphite flakes, paraformaldehyde (reagent grade), and HTBD were all purchased from Sigma-Aldrich. 1,12-diaminododecane (98% purity) was bought from TCI. Chloroform (99.8% purity) was obtained from Acros whereas H_2SO_4 (96.2% w/w), tetrahydrofuran (THF, 99.9% HPLC grade), and acetone (99.7% purity) were all obtained from Fisher-Scientific. 1 N NaOH solution was prepared by dissolution of pellets of NaOH (Fisher-Scientific, 99.4%) in Milli-Q water (18.2 M Ω cm resistivity). Crystalline NaCl (99.2%-purity) from Fisher-Scientific was used to prepare 0.5 M NaCl aqueous solution. All of the aforementioned chemicals were used as is.

2.2. Substrate preparation

The carbon steel sheets were first cut into 1.5 × 2.0 cm pieces, and ground with increasing grades (400, 600, and 1200) of silicon carbide papers. They were then sonicated in acetone for 15–20 min, dried, and kept under vacuum prior to use.

2.3. Synthesis of BZ monomer

The difunctional linear diamine-based BZ monomer was synthesized [39] through the Mannich reaction of stoichiometric quantities (2:4:1) of phenol, paraformaldehyde, and 1,12-diaminododecane. The first part of the reaction path is shown in Fig. 1. The reactants were dry mixed

and refluxed in chloroform for 16 h at a concentration of 5 mL solvent per gram of reactants. After cooling to room temperature, the crude monomer solution product was washed many times with solution of 1 N NaOH, followed by rinsing with Milli-Q water until neutral. The washed products were dried over anhydrous sodium sulfate overnight and filtered. Chloroform was then removed by rotary evaporation, and the obtained BZ monomer was refrigerated until use.

2.4. Synthesis of GO

GO was prepared using the modified Hummer's method [34]. In a flask, 3 g of graphite flakes, 400 mL of H_2SO_4 , and 3 g of KMnO_4 were mixed. 3 g of KMnO_4 was added every 24 h for 3 days. The reaction was ceased by adding an ample amount of hydrogen peroxide into the mixture. The mixture was centrifuged to collect the solids GO and was repeatedly washed with 2-propanol until the supernatant had a neutral pH. It was then dried under vacuum, ground, and refrigerated until further usage.

2.5. Preparation of coatings

Preparation of the PRG coatings was performed by following the subsequent steps. Firstly, HTBD/BZ solution was prepared by melt mixing 20 wt% of the polybutadiene rubber with the BZ monomer under vigorous mechanical stirring at 100 °C for 2 h. Secondly, HTBD/BZ solution was mixed with varying amounts of GO (0, 0.5, 1.0, 1.5, 2.0, and 3.0 wt%, with corresponding nomenclatures of PR, PRG0.5, PRG1.0, PRG1.5, PRG2.0, and PRG3.0, respectively) dissolved in THF solvent: specifically, this is done by first dispersing GO in THF assisted by ultrasonication; HTBD/BZ solution was added afterwards, and mechanically stirred and ultrasonically mixed for 30 min each before use. In all coatings prepared, 3 g of combined weight of GO and HTBD/BZ solution were mixed per 5 mL of the solvent THF. Thirdly, the substrates were dip-coated into the different coatings for uninterrupted 5 times with a withdraw speed of 100 mm per min. The substrates remained in the solution for 1 min every time. Finally, the THF solvent was evaporated by drying in an oven at 60 °C for 1 h followed by curing of the coated substrates at 200 °C for 2 h. This curing process polymerizes the multifunctional BZ monomers resulting in the formation of thermosetting PBZ. The polymerization reaction is shown in Fig. 1. The coatings, upon curing, were estimated to have a thickness of 50 μm .

2.6. Instrumentation

The Fourier Transform Infrared (FT-IR) spectroscopy was done with Cary 600 Series FTIR Spectrometer (Agilent Technologies) and scanned between 4000 and 400 cm^{-1} . All spectra were recorded with nominal spectral resolution of 2 cm^{-1} and 128 scans were collected and averaged for each spectrum. Raman spectra were collected using i-Raman Plus (B&W TEK Inc.) with an excitation wavelength of 532 nm. Thermal stability of the nanocomposites was studied using a TGA 2050 Thermogravimetric Analyzer (TA Instruments) under a continuous nitrogen purge at 110 mL/min. Weight loss was monitored as 5–10 mg samples of the nanocomposites were heated at a rate of 10 °C/min to a maximum temperature of 700 °C.

Static water contact angle was measured by using a CAM 200 Optical Contact Angle Meter (KSV Instruments Ltd.). Adhesion test measurement was performed according to the ASTM standard test method D-3359 for measuring the adhesion strength by tape test. A blade handle equipped with a four-tooth 2.4-mm spacing coarse blade was used to make the cross-cut configuration through the coatings. The coating was brushed lightly with a soft brush after each cut to remove any debris, detached flakes, or ribbons of coatings from the surface. Scotch tape 51596 was placed on the cut surface and rubbed with the pencil eraser-end to provide a guaranteed contact with the coating and then removed quickly after 90 s. The grid areas were inspected for

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