



Unique coating formulation for corrosion and microbial prevention of mild steel



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ARTICLE INFO

Article history:

Received 20 March 2013

Received in revised form

16 November 2013

Accepted 6 December 2013

Available online 25 December 2013

Keywords:

Nano-hybrid coating

Capacitive behaviour

TGBAPB epoxy resin

Corrosion prevention

Anti-bacterial

Surface functionalized nano ZnO

ABSTRACT

TGBAPB matrix material along with functionalized (F-ZnO) and non-functionalized (N-ZnO) nano ZnO as reinforcements was used to develop two unique skeletally modified tetra functional epoxy nano-hybrid coatings. The formation of N-ZnO was confirmed by TEM analysis. Amine functionalization of ZnO nanoparticle on its surface was achieved by grafting 3-aminopropyltriethoxysilane (APTES) as coupling agent. The FT-IR spectra revealed that the silane coupling agent was covalently bonded to the surface of ZnO nanoparticles, offering better dispersibility and compatibility with TGBAPB epoxy matrix. The effect of surface functionalization of nano ZnO towards corrosion resistance investigated by electrochemical impedance (EIS) indicates that the coating film had good corrosion resistance. Furthermore, the antimicrobial test indicated that F-ZnO-TGBAPB coating had strong antimicrobial activity against high concentration of *Escherichia coli* (Gram-negative) bacteria. Thus the TGBAPB-F-ZnO coating formulation appears to be unique by preventing both corrosion and bacterial growth.

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1. Introduction

The versatility along with cost effectiveness of mild steel has led to its utilization in myriads of fields like marine, chemical processing, petroleum production, mining, construction, etc. The major drawback of mild steel is its limited resistance to corrosion. Interest on the deterioration of infrastructure exposed to marine environments, studying the rate of loss of strength of steel and consequent loss of material in infrastructure system is on the rise [1]. India loses more than \$40 billion a year – about 4% of the size of the total economy – due to corrosion in infrastructure and industry segments [2]. Epoxy resin has been widely used as a coating material to protect the steel structures and, submerged structures because of its outstanding salt–water resistance, good insulating properties, and strong adhesion/affinity to heterogeneous materials [3–5]. Epoxy coatings generally reduce the corrosion of a metallic substrate subject to an electrolyte in two ways. First, they act as a physical barrier layer to control the ingress of deleterious species. Second, they serve as a reservoir for corrosion inhibitors to aid the steel surface in resisting attack by aggressive species such as chloride anions. Nonetheless, the successful application of epoxy coatings is often hampered by their susceptibility to damage by

surface abrasion and wear [6,7]. They also show poor resistance to the initiation and propagation of cracks [8]. Such processes introduce localized defects in the coating and impair their appearance and mechanical strength. The defects can also act as pathways accelerating the ingress of water, oxygen and aggressive species onto the metallic substrate, resulting in its localized corrosion.

Furthermore, epoxy coatings experience large volume shrinkage upon curing and can absorb water from surroundings [9,10]. The pores in the cured epoxy coating can assist in the migration of absorbed water and other species to the epoxy–metal interface, leading to the initiation of corrosion of the metallic substrate and subsequently to the delamination of the coating. The barrier performance of epoxy coatings can be enhanced by the incorporation of a second phase that is miscible with the epoxy polymer, by decreasing the porosity and restraining the diffusion path for deleterious species. For instance, inorganic filler particles at nanometer scale can be dispersed within the epoxy resin matrix to form an epoxy nanocomposite coating. The incorporation of nanoparticles into epoxy resins offers environmentally benign solutions to enhance the integrity and durability of coatings, since the fine particles dispersed in coatings can fill cavities [11–13] and cause crack bridging, crack deflection and crack bowing [14].

Functionalization of nanoparticles can also prevent epoxy disaggregation during curing, resulting in a more homogenous coating. Nanoparticles tend to occupy small hole defects formed from local shrinkage during curing of the epoxy resin and act as a

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bridge interconnecting more molecules. This results in a reduced total free volume as well as an increase in the cross linking density [15,16]. In addition, epoxy coatings containing nanoparticles offer significant barrier properties for corrosion protection [17,18] and reduce the trend for the coating to blister or delaminate. In recent years, the use of antimicrobial agents in surface coatings has been increasing to control the growth of bacteria and fungus in bio-medical coatings and adhesives. Considerable attention has been paid to the utilization of epoxy resin as antimicrobial coatings [19–22] for steel substrate has been demonstrated [23–27]. Epoxy antimicrobial coatings are of great interest for protection of surfaces, since survival of microorganisms on surface environment can be detrimental to the materials. Therefore, the development of epoxy nano structured coatings with antimicrobial properties is essential. Zinc oxide (ZnO) belongs to a group of metal oxides with photo-oxidizing and photo-catalytic ability against chemical and biological species [28]. It is an inorganic white powder and is insoluble in water. ZnO nanoparticles have been shown to offer useful antibacterial and antifungal properties when used in surface coating on materials and textiles [29]. Zinc is an essential element and ZnO nanoparticles are considered to be non-toxic as well. Toxicity studies have shown that zinc ions do not cause any damage to the DNA of human cells [30]. A study by Yamamoto in the year 2001 [31] to evaluate the antibacterial activity of ZnO with particle sizes of about 10–50 nm showed superior antimicrobial behaviour than bulk ZnO particles with a size of 2 μm . The antibacterial activity of ZnO nanoparticles is due in part to their electrostatic interaction with cell surfaces. The research reported by Sharma et al. in the year 2010 [32] showed that the cytotoxic behaviour of ZnO nanoparticles ruptures the lipid bi-layer of bacterium resulting in leakage of cytoplasmic contents on contact with bacteria. Owing to the above properties exhibited by nano ZnO, we chose nano ZnO as reinforcing additive for our present study. This work examines the effect of surface functionalized (F-ZnO) and non-functionalized (N-ZnO) ZnO nanoparticles on a skeletal modified tetra functional TGBAPB epoxy nano structured coating. This study also focuses on antimicrobial and anticorrosion behaviour of such coatings. We believe that this work may provide proper guidance for the design of high functionality epoxy nano structured coatings that are seldom explored for corrosion and antibacterial protection of steel substrates. Here we have managed to develop a nano structured-hybrid coating formulation based on tetra functional epoxy resin reinforced with surface functionalized nano ZnO (F-ZnO), which prevented both corrosion and bacterial growth together to a considerable extent. This dual behaviour exhibited by surface functionalized nano ZnO is corroborated by experimental evidences.

2. Experimental

2.1. Materials

All chemicals are reagent grade and were used without further purification except dimethylformamide (DMF), which was purified by distillation under reduced pressure over calcium hydride. Hydroquinone, *p*-chloronitrobenzene, potassium carbonate (K_2CO_3), polyethylene glycol, zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$), ammonia solution, absolute ethanol, hydrazine hydrate (80 wt% water solution), 10% palladium (Pd/C) on activated carbon, epichlorohydrin (EPC), benzene and sodium hydroxide (NaOH) were obtained from SD fine chemical company, India. Silane coupling agent 3-aminopropyltriethoxysilane monomer commercially called as KH550 (at a purity of 99.8%), acetone and *o*-xylene were purchased from Sigma–Aldrich, India. Aradur 140 (polyamidoimidazoline) curing agents were obtained from Huntsman (India). Muller Hinton

agar and the Muller Hinton broth were procured from Himedia, India.

2.2. Synthesis of TGBAPB via BNPB

1,4'-Bis (4-nitrophenoxy) benzene, (BNPB) was synthesized by the reaction of hydroquinone (0.20 mol) and *p*-chloronitrobenzene (0.44 mol) in DMF (300 ml) in the presence of potassium carbonate (0.44 mol). The mixture was heated to 145–150 °C under N_2 atmosphere, and then kept about 8–10 h. After cooled to the room temperature, the mixture was poured into the mixture of water/ethanol (1/1, v/v) and filtered to give a solid product, which was recrystallized from ethanol. BNPB (0.20 mol), 0.78 g Pd/C and 600 ml ethanol were introduced into a 1000 ml three-necked round bottom (RB) flask to which hydrazine hydrate (85 wt%, 182 ml) was added drop wise over a period of 1 h at reflux temperature, after that the reaction was continued for about 5 h. The mixture was then filtered to remove the catalyst, after cooled to the room temperature [33]. The product was precipitated to obtain 1,4'-bis (4-amine-phenoxy) benzene (BAPB) and the sequence of reactions involved is given in Scheme 1. The tetraglycidyl 1,4'-bis (4-amine-phenoxy) benzene (TGBAPB) resin was synthesized using EPC and BAPB with 40% NaOH solution [34]. A pale brown coloured resin TGBAPB obtained (yield 80%) was purified and preserved for further use.

2.3. Synthesis of nano ZnO

The nano sized ZnO (N-ZnO) was synthesized by homogeneous precipitation method followed by calcination as mentioned in the previous work [35]. Firstly, polyethylene glycol solution was syringed into a three-neck flask. Then, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{CO}_3$ aqueous solutions were dropped into the flask at the same time with vigorous stirring. After reacting for 2 h at room temperature, the precipitates were washed and filtered with ammonia solution (pH 9) and anhydrous ethanol for several times, and dried under vacuum for 12 h. Finally, the precursors were calcined in an oven at 450 °C for 3 h and milled, and then ZnO nanoparticles were obtained.

2.4. Surface functionalization of nano ZnO

The introduction of reactive NH_2 group onto the surface of nano ZnO was achieved through the reaction between 3-aminopropyltriethoxysilane and the hydroxyl groups on the nano ZnO surface. Typically, 2.0 g nano ZnO and 2 ml 3-aminopropyltriethoxysilane in 40 ml *o*-xylene were kept at 150 °C for 3 h under stirring and argon protection. After that the amine functionalized nano ZnO was collected by filtration and rinsed three times with acetone. Afterwards, the amine functionalized nano ZnO was dried under vacuum for 12 h [36]. The reaction sequence is given in Scheme 2.

2.5. Preparation of functionalized nano ZnO/TGBAPB epoxy coatings

TGBAPB epoxy was mixed separately with N-ZnO and F-ZnO (2.5 wt%) at 60 °C for 15 min, with constant stirring and stoichiometric amount of curing agent was added as a room temperature Aradur 140 (Table 1). This formulation was applied on mild steel specimen to a thickness of 100 μm using bar coater. The samples were kept for 7 days to allow complete curing. Finally the specimens were tested for their corrosion and antimicrobial properties. The method of application is shown in Fig. 1. The functionalized nano ZnO (F-ZnO) forms a covalent bond with TGBAPB epoxy resin as shown in Scheme 3.

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