Journal of Science: Advanced Materials and Devices xxx (2016) 1–12

Contents lists available at ScienceDirect

Journal of Science: Advanced Materials and Devices

journal homepage: www.elsevier.com/locate/jsamd

Original article

Design and characterization of non-toxic nano-hybrid coatings for corrosion and fouling resistance

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ARTICLE INFO

Article history:
Received 23 June 2016
Received in revised form
4 July 2016
Accepted 4 July 2016
Available online xxx

Keywords:
Epoxy
Nano-hybrid coatings
Anticorrosion
Antimicrobial
Antifouling

ABSTRACT

Epoxy resin modified with nano scale fillers offers excellent combination of properties such as enhanced dimensional stability, mechanical and electrical properties, which make them ideally suitable for a wide range of applications. However, the studies about functionalized nano-hybrid for coating applications still require better insight. In the present work we have developed silane treated nanoparticles and to reinforce it with diglycidyl epoxy resin to fabricate surface functionalized nano-hybrid epoxy coatings. The effect of inorganic nano particles on the corrosion and fouling resistance properties was studied by various (1, 3, 5 and 7 wt%) filler loading concentrations. Diglycidyl epoxy resin (DGEBA) commonly was used for coating. 3-Aminopropyltriethoxysilane (APTES) was used as a coupling agent to surface treats the TiO_2 nanoparticles. The corrosion and fouling resistant properties of these coatings were evaluated by electrochemical impedance and static immersion tests, respectively. Nano-hybrid coating (3 wt% of APTES–TiO_2) showed corrosion resistance up to 10^8 Ω cm^2 after 30 days immersion in 3.5% NaCl solution indicating an excellent corrosion resistance. Static immersion test was carried out in Bay of Bengal (Muttukadu) which has reflected good antifouling efficiency of the 3 wt% APTES–TiO_2 loaded nano-hybrid coating up to 6 months.

1. Introduction

In recent years, with the development of nano technology, researchers try using nano size fillers to modify epoxy resins. The nanoparticle reinforced epoxy resins show huge improvements on their properties due to the unique characters of nano size fillers [1,2]. Currently people believe that the improvements of epoxy resins' properties are the result of nano size particles' surface effect, quantum size effect and macroscopic quantum tunneling effect [3]. Because of the high viscidity of epoxy resin, it is hard to mix nano size fillers uniformly into epoxy resins. So it is also necessary to consider the manufacture process. Corrosion protection of metallic substrates was one of the important roles performed by organic coatings. Such coatings remain cost-effective for many users who would like to have substrates coated just once and assume appearance and function to be maintained. Organic coatings are often used as a protective layer over the metal substrate to prevent the substrate from oxidizing in a manner deleterious to the function and appearance of an object. They do so in several ways [4]. First, they act as a barrier limiting the passage of current necessary to connect the areas of anodic and cathodic activity on the substrate. This occurs especially if the coating wets the substrate surface very well and has good adhesion in the presence of water and electrolyte. Coatings do not really stop oxygen sufficiently to make concentrations at the surface rate limiting and they do not completely stop water ingress into them. However, a good barrier coating slows water and electrolyte penetrations and is not displaced by water at the substrate/coating interface.

Furthermore, 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 zigzagging 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 nano-hybrid 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 thoroughly in coatings can fill cavities [5–7] and cause crack bridging, crack deflection and crack bowing [8]. Nanoparticles can also prevent epoxy

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Peer review under responsibility of Vietnam National University, Hanoi.

http://dx.doi.org/10.1016/j.jsamd.2016.07.001

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 bridge interconnecting more molecules. This results in a reduced total free volume as well as an increase in the cross-linking density [9,10], In addition, epoxy coatings containing nanoparticles offer significant barrier properties for corrosion protection [11,12] and reduce the trend for the coating to blister or delaminate.

In recent years, a rapid surge of "green" metal pre-treatment technology based on the silane agents was found in the field of corrosion control of metals. The silane coupling agents have a general structure of $(XO)_3SiY$, where XO is a hydrolyzable alkoxy group, which can be methoxy (OCH_3) or ethoxy (OC_2H_5) and Y is an organofuctional group. The formation of silane films is based on the condensation reactions between silanols (Si-OH, hydrolysis product of alkoxy group) and the metal hydroxyls (Me-OH). The organofuntional silane films deposited on the metal are usually hydrophobic. They can act as a physical barrier against water. In addition, the silane films can also act as adhesion promoters between metal substrate and organic coatings. In the past decade many studies were done in corrosion protection properties of such silane films [13–15].

In addition to the anticorrosion properties of epoxy nanohybrid coatings they have enhanced an antimicrobial property that is useful in marine applications. Marine microbiological corrosions are responsible for considerable damages to all devices and vessels immersed in seawater, and this induces serious economic problem to maritime activities [16]. Employing effective antifouling marine paints, containing booster biocides at non-toxic levels is one approach to solve the issue of fouling [17]. One important function of paints containing biocides or inhibitors is to obtain optimal release rate of the actual active substance into the sea. The leaching rate of biocides should not be too fast, resulting in rapid and premature depletion of the antifouling activity of marine coatings and unnecessarily high concentration in the sea. However, the release rate should not be too slow since this would undoubtedly result in fouling [18]. In order to deal with both issues, application of core–shell structured materials should be one of the best alternatives since the shells offer protection to the cores and introducing new properties to the hybrid structures [19]. With all these thoughts in our mind, we made an attempt to develop a unique epoxy coating formulation having functionalized nano scale filler reinforcement capable of offering both corrosion and microbial prevention.

2. Experimental

2.1. Materials

The base materials used in this work are di functional epoxy resin (DGEBA) and Aradur HY951 triethylenetetramine (TETA) – a room temperature curing agent, which is used in all the systems supplied by Huntsman Advanced Materials. 3-aminopropyltriethoxysilane and all other reagents were purchased from Sigma–Aldrich chemicals and used without further purification.

2.2. Methods

The FT-IR spectra were recorded on a Perkin Elmer 781 FTIR spectrometer that determines the chemical bonds on TiO_2 and APTES. Spectra of nano-hybrid coatings were obtained with KBr pellets. Vibration bands were reported as wave number (cm^{-1}). The TiO_2 particles were characterized by X-ray diffraction (XRD) was equipped with a Copper target ($\lambda = 1.5405$ Å) radiation using Guinier type camera used as focusing geometry and a solid state detector. Curved nickel crystal was used as the monochromator to produce Cu $K_{\alpha 1}$ radiation in the range of 20°–90°. A JEOL JEM-3010 analytical transmission electron microscope, operating at 300 kV with a measured point-to-point resolution of 0.23 nm, was used to characterize the spherical morphology of unmodified TiO_2 and modified TiO_2. The same samples were then coated with a thin layer of gold by vaporization and morphology was observed by scanning electron microscope (LEO 1455VP). Atomic force microscopy (AFM) image of the samples was performed in the air with a digital Instrument AGILENT – NP410A series 5500 AFM in contact mode. Dispersion stability of nanoparticles (untreated and treated) was evaluated in an organic solvent in order to achieve proper dispersion of nanoparticles in the epoxy-based coating and making possible chemical interactions between nanoparticles and polymeric coating. These are then to be subjected to electrochemical impedance and salt-spray analysis to ascertain their corrosion resistance behavior. Isolated microbes and their antimicrobial activity were carried out on epoxy nano-hybrid coatings by agar diffusion technique. Fouling resistance of the coatings was determined by antifouling studies by subjecting the coated samples in sea for a period of 12 months at east coast of India, Tamil Nadu, Chennai (Muttukadu boat house). The interesting results obtained from this investigation are discussed in detail with supporting evidences.

2.3. Synthesis of TiO_2 nanoparticles

For the synthesis of TiO_2, 0.5 M titanium butoxide solution was prepared in 100 ml butanol and stirred for 15 min; further 30 ml DI water was added drop wise in the above solution to allow hydrolysis. This solution was stirred for 30 min, which gave rise to white precipitation. The obtained white precipitate was microwave irradiated for 5 min at 700 W power using microwave system. The microwave used for this experiment was having a power range of 140–700 W. This obtained solution was left 24 h for aging at room temperature and then centrifuged at 2000 rpm for 15 min. Obtained precipitate was dried at 80 °C for 12 h. After complete drying, powder was crushed and calcinated in air at 500 °C for 2 h to remove hydroxide impurities and recrystallization.

2.4. Synthesis of APTES grafted TiO_2 nanoparticles

0.5 g of TiO_2 nanoparticles was dispersed in 50 ml DI water by ultra-sonication for 10 min. Then, the silane coupling agent APTES with concentrations (5 g) were added in the dispersion. After that, dispersed particles were separated from solvent by centrifuge (10 min at 10,000 rpm) followed by washing with ethanol and water alternatively for at least 2 cycles to remove excessive silanes. To re-disperse the centrifuged particles in fresh solvent, they were put in ultrasonic bath for more than 10 min to make sure a visually well dispersed suspension was regained before centrifuge again. Once the process was finished, the modified particles were dried in an oven at 100 °C for 24 h and cooled in a vacuum chamber for 1 h at room temperature.

2.5. Synthesis of TiO_2–APTES–DGEBA nanohybrid coatings

Epoxy coating was prepared using a high speed disperser. The fabrication processes of TiO_2–APTES–DGEBA mixtures were as follows. Different weight percentages of APTES grafted TiO_2 nanoparticle (0, 1, 3, 5 and 7 wt%) were directly added to vessel charged with epoxy resin and solvent mixture (butanol/xylene) followed by addition of additives. The pigment was dispersed by stirring at 400 rotations per minute (RPM) for 30 min and then

Please cite this article in press as: P. Saravanan, et al., Design and characterization of non-toxic nano-hybrid coatings for corrosion and fouling resistance, Journal of Science: Advanced Materials and Devices (2016), http://dx.doi.org/10.1016/j.jsamd.2016.07.001