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Comparative study of effect of corrosion on mild steel with waterborne polyurethane dispersion containing graphene oxide versus carbon black nanocomposites

G. Christopher[a], M. Anbu Kulandainathan[b], G. Harichandran[a,*]

[a] Department of Polymer Science, University of Madras, Guindy Campus, Chennai 600025, India
[b] Electro-Organic Division, Central Electrochemical Research Institute, Karaikudi 630006, India

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ABSTRACT

Recently developed strategies for graphene oxide and carbon black nanocomposites have enabled production of robust waterborne polymer nanocomposites with enhanced nanoparticle dispersion and barrier protection performance. In this article, we have presented processing, morphology and properties of waterborne polyurethane (WPU) reinforced with synthetic polymer of polyvinyl alcohol (PVA) modified GO/zinc oxide (GO/ZnO) and functionalized carbon black/ZnO (CB/ZnO) nanocomposites. The incorporation of nanofillers into PVA matrix offers the opportunity to develop nanocomposites with enhanced anchoring effect and barrier protection properties. For the first time, we have compared CB and GO nanocomposites for its corrosion protection, latter was found to be superior in resistance to corrosion than former. The prepared nanocomposites were characterized by XRD, FESEM, XPS, Raman spectroscopy and contact angle measurements. The corrosion resistant properties were investigated by potentio-dynamic polarization studies using Tafel parameters and electrochemical impedance spectroscopy. Incorporation of 0.1–0.3 wt% of nanofillers in WPU dispersion has produced effective nanocomposite, with a resistance to corrosion on mild steel. This observation is in good qualitative agreement with the surface wettability and dispersion level of the nanocomposite in waterborne medium. This study has showed a new approach for synthetic polymer PVA anchored GO/ZnO and CB/ZnO which acts as filler in waterborne medium enhances the anti-settling behavior and resistance to corrosion. Moreover, by comparing these results reveal that, PVA anchored GO supported nano ZnO is higher in performance than PVA anchored CB supported nano ZnO in WPU dispersion.

1. Introduction

Corrosion of metals, such as steel, aluminum, copper, etc., occurs when they are expose to aqueous environment is one of the serious problems in the chemical, shipping and manufacturing industries [1–10]. There are three approaches used for corrosion prevention, which are cathodic, anodic and barrier protections. In barrier protective coatings (e.g., paints), metal oxides nanoparticles are generally used as a filler additives, in which they act as a barrier to prevent moisture or oxygen transportation pathways [11–14]. Recently developed water-based polymer coatings containing metal oxide nanoparticles are interesting approach for barrier protection against corrosion.

WPU dispersions are binary colloid system in which polyurethane particles are dispersed in water medium. The development of WPUs is motivated primarily by environmental considerations and also economical aspect. Other advantages are solvent, stain, chemical resistance, toughness with flexibility, environmental safety, good adhesion and rheology characteristics. The addition of various nanoparticles in newly developed coatings provides a wide range of opportunities to improve performance of the coatings (optical clarity, scratch, mar resistance and barrier properties including corrosion resistance and mechanical properties) [14–19].

Most commonly used nanoparticles in coatings for the last two decades are clay, SiO_2, TiO_2, ZnO, Al_2O_3, Fe_2O_3, etc. Each nanoparticles has some unique properties like UV blocking, scratch and abrasion resistance, corrosion protection, etc. [20–27]. All these properties are being achieved by better dispersion capability of nanoparticles in polymer medium which leads to a uniform distribution that enables to fill the pores and increase the crosslinking

* Corresponding author.
E-mail address: umghari@gmail.com (G. Harichandran).

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density of the coating, will enhance the material performance [27]. The main problem with nanocomposites coatings is their lack of dispersion stability due to their high surface activity. This has been overcome to some extent by using chemical or electrochemical treatments onto the surfaces of nanoparticles.

During the last decade the carbon-based material, graphene has been used for many industrial applications, due to its excellent electrical, mechanical and thermal properties, such as polymer composites, energy-related materials, sensors, field-effect transistors and biomedical applications [28,29]. Graphene oxide, which is generated from graphite oxide, has been a promising route to achieve mass production of graphene. Graphene oxide is chemically similar but structurally different to graphite oxide by sonicating or stirring graphite oxide in water and other polar media, which exfoliate to graphene oxide. GO has chemically reactive oxygen functionalities, such as carboxylic acid at their edges and epoxy and hydroxyl groups on the basal planes. GO, which is electrically insulating, can be converted to conducting graphene by chemical reduction [30,31].

The other interesting area of carbon-based materials is carbon black. It is a black pigment which consists of 97–99% elemental carbon and thus is hydrophobic in nature. It has excellent chemical stability, weatherability and colorability that has been utilized in paints, plastics, rubber, printing inks, etc., Though carbon black finds application in paint industry, super capacitors, chemical sensors, fuel cells, etc., the interaction between the particles while dispersing it in a polymer medium it tends to agglomerate, due to Vander Waals force and electrostatic forces of this fine particles which affects them for its coloring and hiding power [32–41]. Comparitively both CB and GO in coating industry finds difficulty to attain a uniform dispersion in polymer matrix by mechanical mixing method.

PVA is a water-soluble synthetic polymer with a high hydrophilicity, good biocompatibility and non-toxicity. PVA is used in warp sizing, paper coating agents, adhesives, carriers in drug delivery and as a component of biomedical and packaging material. The mixing of PVA with inorganic fillers is generally carried out to improve its properties. One of the popular filler is carbon material, which can be used in various polymorphic forms, such as carbon black, carbon spheres, carbon soot, carbon nanotubes, graphite, graphite oxide and graphene [41–47].

The polymer matrix and the filler are bonded to each other by weak intermolecular forces and chemical bonding is rarely involved. If the reinforcing material could be dispersed on a molecular scale and interacted with the matrix by chemical bonding, then significant improvements in the mechanical properties of the material or unexpected new properties might be attained. In that sense, graphite to be converted as GO and CK to be converted as CB, has been successfully coated with ZnO to improve their interaction with polymeric matrices. The chemistry of PVA to form both intra- and inter chain hydrogen bonding with polymer and fillers, could be used as a model for understanding the anchoring effect of filler with polymer to improve the dispersion without aggregation of the nanofiller in the polymer medium.

Recently researchers studied the effects on various metal and its metal oxide nanoparticles, such as ZnO, Ag, TiO_2, etc., supported by carbon materials like carbon sphere, multi-walled and single walled carbon nanotube, carbon soot, fly ash, graphene, GO, reduced GO [48–55]. On other way, polymers reinforced carbon materials have also been studied for last two decades to improve the thermal, mechanical properties of various nanocomposites. But, very few literatures reported carbon materials reinforced polymer and various metal oxide nanoparticles involved nanocomposites for antimicrobial, photo catalytic activity and other thermal properties [56,57]. These materials can also be used as a barrier protection filler to prevent metals from corrosion.

The novelty of this proposed work is to bring a new nano structured materials which acts as filler and is incorporated in to waterborne polymer medium used to enhance the barrier protection efficiency by filling the pores of the coating and restrict the penetration of corrosive species to reach the substrate. This nano structured materials gave good interactions with waterborne medium as well as improve the nanoparticle dispersion simultaneously enhance the protection of metals from corrosion. The uniqueness of this work is to utilize easily available materials as cost effectively in terms of raw material as well as processing and coating applications.

Here, we have reported the novel preparation of two different carbon-based nanocomposites anchored by synthetic polymer and evenly dispersed in WPU medium. The effectiveness of the prepared nanocomposites has been discussed for its processing, morphology, surface wettability and its protection efficiency. PVA anchored GO modified ZnO (PVA/GO/ZnO also denoted as PGZ) and PVA anchored functionalized CB modified ZnO (PVA/CB/ZnO also denoted as PCZ) composites have been prepared. Those composites were dispersed in WPU dispersion with various dosages using solution blending method and were coated on mild steel to study the corrosion protection behavior. We aimed to obtain WPU composites with enhanced nanoparticle dispersion and resistance to corrosion and the results indicated better dispersion and corrosion protection for WPU/PGZ composites than WPU/PCZ.

2. Experimental

2.1. Materials

Graphite flakes and carbon black were purchased from Loba chemicals and Alfa-aesar. Hydrochloric acid (HCl), 98% sulfuric acid (H_2SO_4), 30% hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), zinc acetate, sodium hydroxide, cetyl ammonium bromide (CTAB), nitric acid (HNO_3), polyvinyl alcohol, sodium nitrite ($NaNO_3$), absolute ethanol, methanol and acetone were purchased from Aldrich Chemicals. WPU dispersion (PU-687) was procured from Piccassian Polymers, India. All chemicals were analytical grade and used without further purification. Double distilled water was used throughout this study.

2.2. Synthesis of graphite oxide

Graphite oxide was synthesized from natural graphite by a modified Hummers method (reported procedure with slight modification) [58]. Briefly, 2 g of graphite powder and 1 g of $NaNO_3$ were mixed and then added into 96 mL of concentrated H_2SO_4 with an ice bath. The bath was maintained at a temperature below 20 °C, under vigorous stirring and then 6 g of $KMnO_4$ was added gradually. The ice bath was then removed and the reaction mixture was stirred at room temperature for 18 h. The mixture became pasty with a brownish color immediately. 150 mL of H_2O was slowly added to the pasty mixture. Addition of water into the concentrated H_2SO_4 medium is an exothermic, so keeping the mixture in an ice bath to keep the temperature below 50 °C. After dilution with H_2O, 5 mL of 30% H_2O_2 was added to the mixture. The color of diluted solution changed to brilliant yellow along with bubbling. This mixture was continuously stirring for 2 h then filtered and washed with 10% HCl aqueous solution, De-ionised water and ethanol to remove other ions. The resultant solid was dried by vacuum.

2.3. Preparation of functionalized CB

Carbon black was functionalized according to a reported procedure [36] with slight modification. Carbon black was oxidized with 5 M HNO_3 for 4 h at 90 °C. It was then filtered from solution;