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Development of oxidation and corrosion resistance hydrophobic graphene oxide-polymer composite coating on copper☆

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ABSTRACT

Oxidation and corrosion resistant hydrophobic graphene oxide-polymer composite (GOPC) coating was fabricated on the copper by electrophoretic deposition (EPD). The GOPC coatings were characterized by scanning, and transmission electron microscope (SEM, TEM), thermogravimetric (TGA) and electrochemical impedance spectroscopy (EIS). At optimal EPD conditions of operating voltage 10 V and deposition time 30s, uniform crack free deposit with thickness 45 nm was achieved. Potentiodynamic polarization and EIS investigation demonstrated the efficacy of GOPC coating in shielding copper from corrosion under stringent environment condition. The electrochemical degradation of GOPC coating is more than three orders of magnitude lower than the bare copper substrate. This was due to the impermeability of GOPC coatings to ion diffusion of oxidizing gas and corrosive liquid solution. The procedure employed is fairly facile, inexpensive and less time consuming.

1. Introduction

Majority of industries are inherently faced with the problem of corrosion and steps for protection of materials from corrosion has been of large interest to them. Although many corrosion prevention techniques are in operation, it is necessary to increase the life of the components further. Recently nanocomposite coatings, hydrophobic coatings and organic–inorganic hybrids have been shown to increase the life of materials prone to oxidation/corrosion, resulting in huge saving. Such cutting edge coatings technologies have the market potential for wide range of applications such as marine, pipeline, aerospace, automobiles and construction industries.

The promises shown by nanomaterials and emergence of advance coatings technique have increased the expectation further. Producing robust oxidation and corrosion resistant coatings are the most important requirement by the industry, which can increase the service life of the materials even under severe environmental conditions. Nanostructured materials engineering has enabled the possibility of designing environmental friendly anti-corrosion coatings which can last much longer compared to traditional coatings.

The discovery of graphene, a two dimensional one atom thick sp^2 hybridized carbon nanostructure with its unique characteristic properties such as chemical inertness, thermal and chemical stability, mechanical strength and impermeability to ion diffusion make it very strong candidate for corrosion resistance and protective coating on metal. However, immobilization of graphene directly on metal surfaces is difficult, further graphene has poor dispersibility in either aqueous or nonaqueous solvents [1] poses greater challenges working with graphene. Also, graphene sheets are chemically inert, preventing any kind of interaction with the polymer matrices, that causes extended filler-filler aggregation in composites [2,3]. On the other hand, graphene oxide (GO) consists of a hexagonal carbon network with both sp^2 and sp^3 hybridized carbons with hydroxyl and epoxide functional group on its basal plane, and carbonyl and carboxyl groups on the edges [4,5]. The oxygen bearing functional groups render GO hydrophilic and dispersible in water and polymers. Hence, processing to make GO-polymer composite materials is comparatively easier compared to graphene. During oxidation of graphite to GO, the sp^2 hybridized carbon structure is broken and develops defects by disrupting π-π conjugation and increase the distance between adjacent sheets of graphite from 0.335 nm to 0.68 nm (GO) [6], the increased spacing reduces interaction between sheets, and hence easing out the exfoliation of GO into single layer GO sheets in aqueous media. It has been shown that GO [7] is potentially effective reinforcement [8,9] for nanocomposite materials and used for diverge applications including coatings, as reinforcement potentials increases linearly with filler stiffness and strength [10,11].

There are quite a good number of published work on GO and GO-polymer composites, some select one are summarized briefly. Valentini et al. [12] proposed various methods for the fabrication of transparent functional coatings while preserving the physical properties such as optical transparency and electrical conductivity of the organic–inorganic hybrid systems. Bittolo Bon et al. [13] reported solution

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casting technique for preparation of functional composites by combining aqueous dispersion of alkylated GO nanosheets and PEDOT:PSS polymer and found enhanced electrical conductivity without any detrimental effect on the optical transparency of the polymer. Sangermano et al. [14] reported development of transparent conductive GO/acrylic resin coatings by photopolymerization. GO/PEGDA nanocomposite coatings present a good dispersion of GO sheets inside the polymer matrix. It has been reported that after photopolymerization, the GO flakes undergo excellent conformal filling within the PEGDA cross linked matrix. They further demonstrated that a conductive PEGDA coating can be easily obtained by this technique by addition of GO as low as 0.02 wt%. Santos et al. [1] reported nanocomposite coated film of graphene oxide and poly-N-vinyl carbazol polymer for antimicrobial activities by electrodeposition. The antimicrobial film was 90% more effective in preventing bacterial colonization in comparison to the unmodified surface. Cano et al. [11] reported functionalization of graphene oxide and poly vinyl alcohol (PVC) to prepare paper-like composite materials by vacuum filtration technique, which are much stronger and stiffer than GO only or mixture of GO and PVA. They have shown that GO reinforcement is very useful to increase the strength of the composite materials for coating and other applications. Hu et al. [15] reported simple procedure to prepare large scale graphene papers and their mechanical enhancement by drop casting technique on hydrophobic substrates. The final GO paper can be peeled off easily and the freestanding GO papers can be fabricated in large scale. This has potential applications in many industries including coatings.

One of the well known traditional techniques for the preparation of thin film coating is chemical vapour deposition (CVD). CVD is a high temperature process; growth temperature usually varies from 650 °C to 1000 °C depending on carbon source and nature of substrate, requires high vacuum and has limitation on sample size [16,17]. Therefore, it is of great interest to develop aqueous based environment benign practical technique which allows fabrication of GO bearing thin film coatings that are simple, scalable and cost effective. Electrophoretic deposition (EPD) technique is most appropriate where filler and polymer are well dispersed in either aqueous or organic solvents. In this regard the solution processability of GO and polymeric matrix is very smart preparation technique of polymer composite coatings by EPD technique.

EPD is a promising technique for the fabrication of functionally graded materials [18–20], hybrid composite materials [21,22], laminated nanoceramics [23–25], functional and nanostructured films and coatings [26–28]. For the last couple of year vast arrays of new applications are emerging, this is because EPD has important industrial application and commercial advantages over other fabrication routes. It is a very versatile and cost effective material processing technique, having good control over microstructure, stoichiometry, macroscopic and microscopic dimensions and properties [29,30]. EPD is essentially a two step colloidal forming process in which firstly electrostatically charged particles suspended in a liquid medium migrate under the influence of an electric field towards an oppositely charged electrode, and secondly, the charged particles deposit/flocculated on the electrode forming a relatively dense and homogeneous packed/bonded layer. In this process, it is very convenient to increase the volume fraction of the nano reinforcement. The process is useful for applying materials from submicrons to nanometer scale on any electrically conductive surface. A post deposition treatment is usually required to densify the deposits and to eliminate porosity [29]. Sometime some special post deposition treatment is required to have some specific properties, for example, a special post deposition processing with silicone fluids are made to make the coated surface more hydrophobic and water repellent. There has been growing interest in the use of EPD technique for the fabrication of nanostructured films and coatings for the protection of metals from oxidation and corrosion by providing hydrophobic coating.

The objective of this investigation is to use facile, environment benign aqueous, inexpensive, room temperature EPD technique for GOPC coating on copper. Herein GOPC coating containing GO and polymeric isocyanate crosslinked with hydroxy functional acrylic adhesive as polymer matrix is used to prepare endure oxidation and corrosion resistance composite coating followed by post processing treatment with silicone fluids to impart water repellent hydrophobic property to have overall enhanced protection of copper substrate from electrochemical degradation. The corrosion behavior in an accelerated laboratory condition was evaluated by potentiodynamic polarization and EIS. The corrosion resistance of GOPC coated specimen was more than three times higher than the bare copper substrate.

2. Experimental

2.1. Raw materials

Copper foils used for this investigation was supplied by Sigma-Aldrich, Hyderabad, India. It was used after polishing with SiC paper and ultrasonically cleaned in distilled water and acetone. Graphite powder with purity 99% from Himedia, Mumbai, India was used to make GO by modified Hummer technique [31]. In this process fixed quantity of graphite was added in conc. H_2SO_4 and $NaNO_3$ solution at 0 °C. While maintaining vigorous stirring, $KMnO_4$ was slowly added to the flask and the temperature was kept below 15 °C. The mixture was stirred at 35 °C until it became pasty brownish, and further diluted with de-ionized water and stirring was continued for another 15 min. H_2O_2 (30 wt%) solution was slowly added into the mixture after which the colour of the mixture changed to bright yellow. The mixture was centrifuged and washed with 1:10 HCl solution for several times to remove the residual metal ions. The powder was dried at room temperature in vacuum desiccators before use.

Polymeric isocyanate crosslinked with hydroxy functional acrylic adhesive was used as polymer matrix. Hereafter polymer matrix is designated as PIHA. A methyl hydrogen silicone fluid supplied by ShinEtsu Chemical Co. Ltd, Tokyo, Japan (trade name KF-99), was used as post deposition treatment to improve water repellency. In addition to increasing water repellency, KF-99 as post deposition treatment is expected to exhibit good heat resistance properties, and stability against thermal oxidation. Unless otherwise mentioned, the other reagents were of analytical grade and were used as received. All aqueous solutions were prepared with ultrapure water (> 18MΩ) from a Milli-Q plus system (Millipore).

2.2. Experimental

In presence of polymer PIHA, GO acquired high positive charge and optimum dosages of PIHA to form a stable suspension was 0.4 mg/g of GO in aqueous medium [32]. An aqueous dispersion of graphene oxide was prepared with concentration 0.01–0.1 g/l with optimum dosages of PIHA. A homogeneous aqueous dispersion of GO and polymer was obtained by magnetically stirring the suspensions at moderate speed for 10 min followed by ultrasonication for 20 min by Vibronic Ultrosonic Processor (Model P2) at 200 V.

Electrophoretic deposition of well dispersed GO/PIHA system on copper was performed using the EPD set-up as depicted in Fig. 1. Two parallel copper plates (9 mm × 30 mm) separated by 10 mm gap were used as the electrodes, one of them works as depositing substrate (cathode) and other as counter electrode. Before each deposition suspension was ultrasonicated for about 20 min. EPD was performed at constant DC voltage mode 10–30 V, employing a source meter (Model: 2410, Keithley Instruments, Inc., USA) with deposition time of 5–50 s. The deposited samples were then carefully taken out from the suspension and allowed to dry overnight at room temperature and weighed to determine the deposit yield. Dried GO/PIHA (GOPC) composite coating commonly known as 'green deposit/body' was treated with silicone fluid (KF-99) to increase the hydrophobicity (water repellency) of the resultant coatings. Silicone fluid (KF-99) was applied by brushing the GOPC coating with fine brush.