Factors affecting barrier performance of composite anti-corrosion coatings prepared by using electrochemically exfoliated few-layer graphene as filler

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ABSTRACT

The electro-exfoliated few-layer graphene (FLG) sheet and epoxy composite systems were studied as model composite coatings. Increasing the loading up to 1 wt% increased the corrosion resistance of the coating by ~20 times, hardness by 30%, elastic modulus by 35% as compared to neat epoxy coating. At a fixed FLG loading, the above mentioned parameters strongly varied with the homogenization time. The mean 'agglomerates' size of FLG in the composite coating decreased from 17.4 μm to 10.6 μm for increasing the homogenization from 10 to 60 min. Correspondingly, mechanical properties of the composite coatings decreased and anticorrosion property increased.

1. Introduction

Polymeric composite coatings form a passive barrier which restricts the corrosive ions to reach the metal surface and hence protect the metal against corrosion. Polymeric coatings are mainly based on epoxy resins due to their high mechanical properties, low shrinkage during curing process, good chemical resistance, high adhesive strength and dimensional stability [1,2]. To enhance the properties of such coatings, composite coatings have been envisaged using fillers of various nature and forms. Therefore, graphene-based nanocomposites such as graphene nanoplatelets (GNPs) [3], graphene nanosheets (GNSs) [4], and graphene oxide (GO) [5] have been exploited as fillers to demonstrate the favorable properties for diverse applications. Epoxy and its composites can be used in different applications such as high-performance nanocomposites of automobiles and aerospace applications where electrical and thermal properties are required. In composite coatings, such as graphene/polymer composites, the enhancement in various properties depends on several parameters such as surface functionalization of graphene [6], interfacial interaction [7], the particle size of graphene [8] and proper dispersion and alignment of graphene fillers in the polymer matrix [9]. All these parameters are interdependent and must work synergistically to improve the properties of any composite coating.

Many studies have been carried out to produce graphene/polymer composites for various applications such as aerospace, automobile and defense industries [10,11]. Obtaining epoxy/graphene nanocomposites with highly dispersed graphene-reinforcements is challenging, which is

the main bottleneck to tap the full potential of graphene reinforcements. The problems with the dispersion of graphene in the matrix arise due to its form factor, high aspect ratio (> 1000) and large specific surface area. An exceptionally large surface area of nano-scale fillers and their quantity in the composite will immensely affect the property due to nano-scale size effect. Ma et al. [12] listed various fillers such as carbon nanotubes (CNTs) and GNP having size less than 100 nm, the surface areas of nano-fillers (carbon fibre) are drastically higher than that of fillers (Al_2O_3 particles) have size of micrometer scale. The surface area of Al_2O_3 and CNT particles differ by 500 times. For example, specific surface areas of Al_2O_3 and CNT particles are 6.0×10^{-8} and 2.8×10^{-5} m^2, respectively [12]. The size of filler also plays vital role in dispersion into the polymer matrix while evaluating its mechanical performance. Feng et al. [13] observed that at 5 wt% small size potassium titanate whisker (PTW) having 0.77 m diameter and 10.47 m length improved mechanical properties and thermal deformation temperature of PTW/PTFE (polytetrafluoroethylene) composites. With increasing filler size, decrement in mechanical properties such as tensile strength, elongation, and hardness were observed. In addition to the size effect, the physical nature of fillers also shows great influence on the dispersion in the matrix. Due to their large aspect ratio and size, fillers exhibit 'restacking' caused by strong van der Waals and 'π–π' interaction. Zaman et al. [14] observed that the morphology and properties of epoxy graphene platelets (GP) nano-composites mostly dependent on the interfacial strength. The GP was synthesized using combined process of sonication and chemical modification. The modified GP (m-GP) was obtained by grafting 4,4′-methylene diphenyl

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diisocyanate (MDI) on GP which subsequently reacted with epoxy matrix during cuthe ring process. The reaction forms a bond between GP and the matrix which enhances the interfacial strength.

The state of dispersion is also the determining factor affecting several properties of the graphene/polymer nanocomposites. The degree of dispersion controls the available surface area of the filler, which affects the neighboring polymer chains and, hence the properties of the bulk nanocomposite [15]. As synthesized graphene sheets usually remain in the form of clusters of graphene ('agglomerates') because of the intermolecular van der Waals force and 'π–π' interaction [16]. The agglomeration leads to poor reinforcement efficiency of graphene in the composites resulting in deteriorated the mechanical performance. That's why the dispersion and exfoliation of graphene in a media have been a pressing issue. Tang et al. [17] studied the effect of the state of dispersion of graphene on the mechanical properties of graphene/epoxy composites. It is also important to control the processing parameters as they affect the homogeneous dispersion of graphene in a composites system. Significant research has been carried out on the manufacturing techniques to achieve homogeneous dispersion. The methods such as solution mixing and resin impregnation are commonly used for epoxy/graphene nanocomposites. In the solution mixing method, a suitable solvent is used for the dispersion of graphene using bath sonication, which imparts strong physical or chemical interaction between the graphene and the polymeric matrices. After this step, the solvent is removed by evaporation process in atmospheric or controlled condition. From the coating point of view, all the above properties are valid. Several factors like particle size, aspect ratio, inherent functionalization are all dependent on the method of the preparation.

Graphene can be synthesized by different methods such as liquid phase exfoliation [18], epitaxial growth or growth on silicon carbide (SiC) [19], chemical vapor deposition [20], chemical synthesis [21] and electrochemical exfoliation method [22–25] etc. Recently, electrochemical exfoliation of graphite has risen very fast, as the process is fast, scalable, cost-effective, and environmentally friendly and yields high-quality graphene. For large-scale production of graphene, the electrochemical exfoliation can be a strongly recommended process as compared to dry and liquid phase exfoliation techniques. However, the composite coating made of graphene produced by this method is rarely investigated and needs proper evaluation.

In this report, we demonstrate the preparation of few layers of graphene (FLG) by electrochemical exfoliation method and its use in epoxy based anticorrosion coating. The electrochemical exfoliation method was optimized to obtain the best possible FLG, based on their layer thickness, defects, and inherent functionality. Such FLGs were used to prepare graphene/epoxy composite coatings for corrosion protection. The physical, mechanical and anticorrosion properties of the coating were evaluated based on the weight percent of the filler, their dispersion state and particle size obtained after varying homogenization time.

2. Experimental

2.1. Materials

Graphite rod ($\phi = 3$ mm), ammonium sulfate ($(NH_4)_2SO_4$) and sodium hydroxide (NaOH) were purchased from Merck Specialties Private Limited, Mumbai, India. Araldite GY250 (Khamir Industries, Mumbai, India), unmodified epoxy resin based on bisphenol-A was used as a polymer matrix having an epoxy equivalent of 183–189 g/eq and density of 1.17 g/cc. The mass ratio between epoxy resin (Araldite GY250) and curing agent (H123, Khamir Industries, Mumbai, India) was 1:1 (wt/wt). Acetone was used as a solvent to reduce the viscosity of the epoxy resin. A mild steel panel was used as a substrate over which coating was applied.

2.2. Synthesis of FLG by electrochemical exfoliation method

Electrochemical exfoliation of graphite was performed using two electrode systems, one is platinum as a counter electrode and other is graphite rod as the working electrode. The 0.1 M ammonium sulfate solution was used as the electrolyte. The pH of the electrolyte was maintained at ~6.5–7 b y using 0.1 M sodium hydroxide solution. The electrochemical assembly was prepared in such a way that graphite rod is fully immersed in an electrolyte. When a DC voltage was applied to graphite rod, the exfoliation of the graphite starts and few-layer graphene (FLG) products are obtained dispersed in the electrolyte solution. A fixed voltage was applied until the completion of exfoliation process of the graphite rod. After the complete exfoliation, the electrolyte color was changed to black due to the dispersion of exfoliated product, this product was collected by centrifugation followed by filtration using Whatman filter paper. The obtained product was repeatedly washed with distilled water to remove the remaining salts. The filtered powder was allowed to dry in a furnace at 60 °C for 12 h. In this study, the DC voltage was varied to study the extent of the exfoliation of the graphite rod. Various DC voltages such as 5, 10, 15 and 20 V were applied to the graphite rod during electrochemical exfoliation process. The application of high voltage on the anode resulted in the gradual exfoliation of graphite through its edges. The time taken by the graphite rod to get completely exfoliated decreased with increasing DC voltage. For different applied DC voltages such as 5, 10, 15 and 20 V, time taken by this process was about 620, 180, 80 and 52 min respectively, for the dimension of the rod used in this work. The yield of exfoliated FLG product was about 97% relative to the initial weight of starting graphite rod.

The schematic representation of the formation process of FLG by electrochemical exfoliation method is presented in Fig. 1. The applied DC voltage causes reduction of water at the cathode, which creates strong nucleophile hydroxyl ions (OH^-). These nucleophiles attack the edge sites and grain boundaries of graphite rod. Oxidation at the edges and at the grain boundaries lead to depolarization and expansion of graphite layers, which facilitates the intercalation of SO_4^{2-} ions between the layers of graphite. During, intercalations of SO_4^{2-}, water molecules also simultaneously intercalate within the graphitic layers. Reduction of SO_4^{2-} ions and self-oxidation of water molecules produce different gaseous species such as SO_2, O_2 and others exert a large force on graphite layers. Hence, weakly bonded graphite layers get separated from each other [26].

2.3. Coating preparation

Here, two sets of composite coatings were fabricated. First set of experiments consists of composite coatings of different FLG loadings such as 0.1, 0.5 and 1.0 wt% on the basis of epoxy resin. Acetone was added to epoxy to enhance the flowability of the mixture. The above mixture was then homogenized using Ultra Turrax T18 homogenizer for 10 min at 500 rpm. Then the mixture was probe sonicated for 10 min using high intensity probe sonicator. The probe sonicator was equipped with a titanium micro-tip of 3 mm diameter and the power was set to 500 W. The intensity was fixed at 100 W. The mixture was then homogenized in the presence of curing agent at 3000 rpm for 10 min in order to achieve a well-dispersed system. The coating was then allowed to settle down for removal of air bubble and then coated on the panels. In a second set of experiments, the effect of varying time of homogenization on 1.0 wt% FLG coating performance was investigated. In this case, the mixture was homogenized for 15, 30, 45 and 60 min after 10 min of using high intensity probe sonication. The operating parameters for probe sonicator were kept same as above. The above mixture was processed under 10 min of homogenization at 500 rpm in the presence of curing agent. Before application of coating, mild steel (MS) panels of dimension $150 \times 75 \times 1.5$ mm were polished with silicon carbide paper of 100 grit (100#) and 1000 grit (1000#) successively.