



# The effect of polycrystalline graphene on corrosion protection performance of solvent based epoxy coatings: Experimental and DFT studies



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## ABSTRACT

In this research, the effect of polycrystalline graphene (PG) on corrosion protection performance of epoxy coating is investigated. Various quantitative and qualitative characterization techniques of X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Porosimetry were employed for characterizing the sample and studying the structure of morphology of the PG. Furthermore, the field emission scanning electron microscopy was considered for investigating the PG dispersion in coating. The corrosion protection performance of epoxy coatings containing different wt.% of PG (0.05, 0.1, 0.3, and 0.5) is evaluated by electrochemical impedance spectroscopy. The results obtained using the prepared nanocomposite showed that the nanocomposite coatings provided higher corrosion resistance compared with the pure epoxy. Meanwhile, nanocomposites containing 0.05 wt% PG show superior corrosion resistance and lower wettability (~12% decrease in water contact angle). The PG sheets agglomerate in matrix by increasing the loading of PG, leading to increase of hydrophilicity and decrease of corrosion protection. Also, the quantum chemical calculations and Density Functional Theory are performed which confirmed the better performance of the epoxy/PG nanocomposite compared with pure samples.

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## 1. Introduction

Corrosion protection of materials is an important issue in the modern metallic finishing industry and advance industrial era [1,2]. To control the corrosion phenomenon and also to prevent the destructive influences of corrosion on economy of nations and industries, researchers have developed a wide range of anti-corrosion techniques [1,3]. Among the various approaches, conventional polymeric coatings such as epoxy coatings have attracted significant attention to protect metallic structures from corrosion; this is due to their magnificent features of low cost, ease of application, and physical barrier properties between the metal surface and corrosive environment [1–4].

However, the drawback of the organic coatings is that they are permeable to corrosive agents which deteriorate their performance. Therefore, nanocomposite coatings are in the center of

attention in order to compensate the shortcomings of polymer coatings [5,6]. Extensive materials including nano-scale inorganic reinforcement materials like silica [7], titania [8], clay [9], carbon nanotubes [2], and graphene [10] have been employed to prepare the modern nanocomposite coatings which are efficient in enhancing the barrier properties of the coatings against electrolyte permeation in the modern composite materials to [11–13].

In this respect, graphene as single-atom-thick sheets of sp<sup>2</sup> bonded carbon atoms is considered an ideal candidate over other conventional nanofillers as it possesses exceptional characteristics including high surface area, high tensile strength, excellent thermal and chemical stability, barrier properties against gases and impermeability to molecules, low density, low viscosity when compounded with polymer, non-toxicity, and low manufacturing cost [14–19]. Graphene sheets can be synthesized by different procedures including micro-mechanical exfoliation of graphite, cleaving graphite by scotch tape, direct exfoliation of graphite in liquid or solid state, chemical vapor deposition of volatile precursors, chemical or thermal reduction of graphene oxide, arc

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discharge method, template route method, electrochemical synthesis, and total organic synthesis [20].

It should be mentioned that graphene with unique inherent properties is used in versatile fields such as photocatalysis [21], light controlled conductive switching [22], bioimaging [23], gas sensing [24], and others. Moreover, researchers showed that the mechanical and barrier properties of epoxy polymers can be improved by incorporating graphene sheets in polymer matrix. From the aspect of mechanical properties, Rafiee et al. [25] directed an investigation on performance of graphene nanosheets and multiwalled carbon nanotubes as nanofiller on mechanical properties of epoxy composites. They showed that epoxy coatings containing graphene nanosheets show significantly better mechanical properties (i.e. tensile strength, Young's modulus, fracture toughness, fracture energy, and resistance to fatigue crack growth) than epoxy/carbon nanotube composite samples. The superior mechanical properties of epoxy/graphene composites can be attributed to high specific surface area of graphene sheets, enhanced mechanical interlocking at interface of graphene and polymer, and the sheet-like structure of graphene. Tang et al. [26] revealed that dispersion state of graphene sheets in epoxy matrix is an important parameter affecting the mechanical properties of epoxy/graphene composites. They found that epoxy composites with highly dispersed graphene sheets show higher glass transition temperature and mechanical strength. Indeed, the well-dispersed graphene sheets can provide fine river-like structure on the fracture surface to consume fracture energy.

In the case of barrier performance, in a research conducted by Chang et al. [14], the graphene nanosheets chemically derived from graphene oxide were used as nanofiller in epoxy coatings; they have reported that by adding 1 wt% graphene nanosheets, the corrosion resistance and hydrophobicity of the epoxy coatings were enhanced which can be assigned to barrier performance and hydrophobicity of the graphene, respectively. In another research, 0.5 wt% 4-aminobenzoyl group-functionalized graphene-like (ABFG) sheets were incorporated into polyaniline coatings by Chang et al. [10] and the corrosion protection of the polyaniline was enhanced. Polyaniline/0.01 wt% graphene nanocomposite coatings were synthesized by Jafari et al. [18] for corrosion protection of Cu surfaces. The graphene dispersed in water containing sodium polyacrylate was used by Liu et al. [27] corrosion inhibiting barrier in waterborne epoxy coating; they reported that the higher corrosion resistance was obtained by epoxy/0.5 wt% graphene nanocomposite coating compared with the epoxy/1 wt% graphene sample.

In this research work, the effect of polycrystalline graphene (PG) on the corrosion inhibiting of the solvent based epoxy coating was studied. Considering the difficulty of synthesizing single crystalline graphene [28], the PG was regarded for enhancing the corrosion protection properties which can be prepared via a relatively simple and low cost chemical vapor deposition (CVD) method on polycrystalline Cu foils [29]. In this synthesizing procedure, the Cu foil grain boundaries act as nucleation sites for individual grains of graphene leading to formation of polycrystalline graphene [28,30]; indeed, PG is composed of numerous single crystalline grains which are separated by grain boundaries [29]. The grain boundaries which can be considered as topological defects influence all the properties of the graphene [31,32]. Further, as distribution of PG layer in the polymer matrix is determining in enhancement of physicochemical property of the nanocomposite in the polymer matrix, the effect of PG wt.% on the corrosion resistance of coatings is considered.

Moreover, Density Functional Theory (DFT) is a powerful tool regarding prediction of chemical reactions which has been recently applied to corrosion protection [33–38]. El-Lateef et al. [39] have performed quantum chemical studies on corrosion inhibition of

some surfactants in which the results were correlated with experimental results. Kaya et al. [40] investigated the benzotriazole and phosphono derivatives as corrosion inhibitor of aluminum in which the results were compatible with those of the experiments. In another research, the functionalized graphene oxide was studied as corrosion inhibitor through experimental and DFT studies. In this regard, the DFT calculations were performed to provide a deeper insight into performance of the prepared materials in corrosion inhibiting.

## 2. Experimental

### 2.1. Materials

Diglycidyl ether of bisphenol A epoxy resin (Epon 1001, epoxy equivalent mass = 480–550, Shell Resin Co.) and polyamide hardener (Versamid 115, amine value = 230–246 mg KOH/g) were used to prepare epoxy coatings. Mild carbon steel plates (ST-12) were purchased from Foolad Mobarakeh Co. of Iran.

### 2.2. PG synthesis

PG is synthesized via CVD method in a quartz tube furnace with methane and hydrogen gas panel on Cu foils (with thickness of 30  $\mu\text{m}$ ) at 1050 °C. After Cu cleaning under flow of  $\text{H}_2$ , methane as carbon source was introduced into the quartz tube and the ratio of methane to hydrogen flow was set as 4:1. The gas flow of methane and hydrogen and the pressure were kept constants as the same values in the PG growth step during cooling step of furnace. After growth of graphene on Cu foil, Cu particles were removed by purification treatments.

### 2.3. Preparation of epoxy/PG nanocomposite coatings

For preparation of epoxy/PG nanocomposites containing different wt.% of PG (i.e. 0.05, 0.1, 0.3, and 0.5 wt%), the PG was dispersed in acetone (0.1 g PG/100 mL acetone) by bath ultrasonic treatment for 1 h and then, the polyamide hardener was added to PG solution. It is worthy to note that the PG was directly added to polyamide hardener with lower viscosity in comparison to epoxy resin in order to enhance the distribution quality of PG nanosheets in polymer matrix [41,42]. The mixture of PG and polyamide hardener was sonicated for 10 min and then heated at 70 °C with magnetic stirring to remove the acetone. In order to remove the entrapped air and also the residual acetone, the obtained mixture was placed in a vacuum oven. In following, by utilizing the high speed shear mixing the epoxy resin was added to the mixture. The prepared sample was diluted with thinner and spray coated on mild carbon steel substrates. Furthermore, the curing process of the substrates was performed at room temperature for 1 week followed by post-curing at 90 °C for 1 h. The thickness of coatings was observed to be in the range of  $150 \pm 10 \mu\text{m}$ . Moreover, the pure epoxy coating was synthesized through mechanically mixing epoxy resin and polyamide hardener in stoichiometric amounts as the reference coating.

### 2.4. Characterizations

The crystal structure of the synthesized PG is characterized by X-ray diffraction (XRD) technique by Bruker D8 Advance ( $\text{CuK}\alpha$ , 40 kV, 40 mA). The morphology and structure of PG were considered by transmission electron microscopy (TEM, JEOL 1200EXII). The surface area, pore volume and pore size distribution were measured by nitrogen adsorption at 77 K using ASAP-2010 Porosimetry from Micrometrics Corporation, GA. The surface area was

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