Comparative Study of Corrosion Properties of Different Graphene Nanoplate/Epoxy Composite Coatings for Enhanced Surface Barrier Protection

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Abstract: Loading of graphene to polymeric materials has proven a widespread increase in the corrosion properties of nanocomposites. In this study, graphene nanoplatelets (Gnps)/epoxy composite coatings were prepared by incorporating three commercial graphene nanoparticles (C750, M15, and X50 Gnps) into epoxy resin. The morphological impact of the Gnps on the surface barrier protection were evaluated in terms of coating’s adhesion to the substate, hydrophobicity and water uptake performance. Salt spray resistance and Electrochemical Impedance Spectroscopy (EIS) authenticated that the coating integrated with C750 Gnp remarkably improved the anti-corrosion performance of neat epoxy composite coatings. A robust passive layer and surface barrier characteristics formed by the composite coatings incorporated with C750 nanoparticle should be the main reason for better protection properties offered by C750 Gnp/epoxy nanocomposites. At the same time, homogeneous dispersion and lesser agglomerates in C750 Gnp/epoxy composite coatings mainly contributed to the coating’s excessive corrosion resistance.

Keywords: graphene nanoplates; epoxy; composite coating; surface barrier properties; corrosion protection

1. Introduction

The problem of metal corrosion has existed since time immemorial, and several attempts have been made to boost the corrosion resistance of metals. Among numerous corrosion protection methods, organic coatings (epoxy based) have gained much interest due to higher corrosion resistance and outstanding adhesion to metallic substrates [1–3]. Nevertheless, epoxy coatings frequently face durability issues such as surface blistering and delamination which is mainly caused by the micro-pores formed during the curing stage of neat epoxy thereby leading to a significant decline in its barrier performance [4,5]. To help curb this problem, many researchers have tremendously tried incorporating nanoparticles in epoxy matrix to enhance its performance. Latterly, Al₂O₃ [6], SiO₂ [7], Ti [8], ZnO [5,9], Fe₂O₃ [10], TiO₂ [11], and graphene nanoplatelets (Gnps) [12] are the most used nanoparticles. Gnps has particularly attained the foremost interest for nanoparticles owing to their exceptional barrier properties [13,14]. Moreover, high specific surface area of Gnps leads to an improved interfacial interaction between the Gnps and the polymeric matrix [14,15]. Additionally, an outstanding electrical, mechanical, thermal conductivity, chemical resistance, hydrophobic nature and impermeability of Gnps proves a greater potential of enhancing the ant-corrosion resistance properties of epoxy composites [16–18].

Recently, several studies have been conducted on epoxy composite coating’s performance incorporated with different nanofillers in various industrial fields [19,20]. For this reason, how Gnps influence the corrosion protection properties of epoxy coatings and its relation to surface barrier improvements is widely investigated. For example, Monet
et al. [21] experimented on the impact Gnps have on epoxy coating’s performance. Their results advised that Gnps improved the corrosion properties of epoxy. In essence, Silvia [22] lately reported that the barrier properties of Gnps/epoxy composites strongly depend on their thickness and lateral dimension in that, a high specific surface area increases corrosion resistance of epoxy coatings once Gnps are uniformly dispersed. Furthermore, the surface barrier properties of Gnps/epoxy coatings have been proven to vary reckoning on the dissimilar topographical features of different Gnp sheets [23]. Liu et al. [24] discussed the corrosion properties of epoxy coating reinforced by graphene nanoparticles. They disclosed that agglomeration of the nanoparticles caused the coating’s surface degradation. On the opposite hand, some authors have also reported on the physical properties of graphene epoxy composite coatings. Satarkova et al. [25] investigated the water uptake performance of composites coatings and concluded that free volume and restriction of polymer chains surrounding the Gnps influenced water absorption. Similarly, Jun [26] evaluated the properties of graphene loaded water-based epoxy coating and discussed that, the presence of graphene did not affect the coating’s adhesion to the metallic substrate but however enhanced the hydrophobic characteristics of the coatings. In fact, it is also proven in recent studies that metal substrates can be well protected by graphene/epoxy films that play a role of physical barrier against corrosion. These findings have been confirmed by some electrochemical measurements indicating that graphene/epoxy coatings hinder the formation of corrosion products [27].

Although Gnps addition in epoxy composite coating has been in the limelight in the field of nano materials, few papers these days addressed Gnps effective utilization and developmental progress with the purpose of enhancing the surface barrier properties of composite coatings against corrosion [5,12,24]. However, the diverse morphological influence of distinct Gnps on the physical surface barrier properties and anti-corrosion protection mechanism of epoxy composite coatings is nevertheless not widely known to the best of our knowledge. In this study, three different commercial Gnps (C750, M15 and X50) with different morphological features were used to prepare Gnps/ epoxy composite coating. Field Emission Scanning Electron Microscopy (FE-SEM), Energy-Dispersive X-Ray Spectrum (EDS) and Optic/Stereoscopic Microscopy were used to characterize the morphology, composition and dispersion characterization of the coatings. Water uptake testing, salt spray testing and electrochemical measurements such as electrochemical impedance spectroscopy (EIS) were employed to determine and analyze the anti-corrosion and water uptake performance of the prepared coatings. The influence mechanism of Gnps on epoxy coating’s anti-corrosion performance was analyzed.

2. Experimental

2.1. Materials

Three different commercial graphene nanoparticles (C750, M15 and X50) were purchased from XG Sciences Inc (Lansing, MI, USA). The physical properties of the Gnps used in this study as provided by the manufacturer is shown in Table 1. The epoxy resin (diglycidyl ether of bisphenol A, E-51) and its Ethylenediamine Hardener were supplied by Shanghai Jiuqing Chemical Co., Ltd (Shanghai, China).

| Grade    | Diameter (μm) | Specific Surface Area (m²g⁻¹) |
|----------|---------------|-------------------------------|
| C750 Gnp | <2            | ~750                          |
| M15 Gnp  | <15           | ~150                          |
| X50 Gnp  | 150           | 50–80                         |

2.2. Preparation of Gnps/Epoxy Coatings on Steel Samples

Chinese GB standard Q235B (DIN EN S235JR European standard) [28] with a chemical composition of (wt.%): C 0.14, Si 0.19, Mn 0.31, P 0.015, S 0.0024, Cu 0.016, and Fe was
used as the main substrate. All samples were immersed in a (H₂O:HCl: methacrylic acid) solution in a ratio of 5:5:1 to remove rust, grounded with (180, 240, 400 and 600) grit abrasive SiC papers, cleaned in acetone for 5 min, washed with distilled water and dried in high-purity nitrogen (99.999%) awaiting to be coated. Pure epoxy coatings were prepared via mechanically mixing epoxy resin and Hardener in the ratio of 3:1. The mixture was degassed in a bath sonicator, coated on the steel substrate and allowed to dry for 24 h at room temperature. To prepare the Gnps/epoxy composite coatings, 1 wt.% of Gnps were added to a measured volume of dimethyl formamide solvent (DMF), ultrasonically dispersed to exfoliate the Gnp sheets in the epoxy matrix with an ultrasonic machine (Ningbo Scientz Biotechnology Co., Ltd (Ningbo, China) at a power of 380 W for 30 min, then vacuum filtered to obtain wet Gnps. According to 4:1 ratio of epoxy and Hardener, a mixed solvent was prepared with the wet Gnps previously obtained. The Gnps/epoxy mixture was ultrasonicated with a power of 100 W for 20 min and then stirred magnetically for 2 h. Finally, the prepared composite coatings were vacuum degassed for 10 min, brush-coated onto the previously prepared steel substrates and allowed to cure for 7 days at room temperature for subsequent test observations. To ensure that the coating layer is of a uniform thickness throughout, good brushing techniques and a flat level surface were employed. Also, the coating was applied liberally and spread uniformly, followed by a criss-crossing action with the brush. The thickness of the dried coatings was measured to be 100 ± 20 μm by sndway SW-6310C coating thickness meter (Shenzhen, Guangdong, China). Figure 1 shows the schematic preparation of the graphene epoxy nanocomposites coatings.

Figure 1. Schematic diagram of the preparation of graphene nanocomposites.

2.3. Characterization of Gnps/Epoxy Composite Coatings

Optical and stereoscopic 3D microscopic images with magnification 200× and 1000× (Bell MPL-1, VHX-500 KEYENCE, Itasca, IL, USA) were taken to investigate the homogeneous distribution of Gnps in epoxy coatings. FE-SEM (ZEISS, Jena, Germany) with
20,000 × magnification and EDS were used to confirm the different morphologies of Gnps and elemental composition of the coatings respectively.

2.4. Pull-Off Adhesion Testing

In order to investigate the coating’s adhesion strength, a pull off adhesion test according to ASTM 4541 standards [29] was employed. All samples were prepared with same procedure as described in Figure 1. Aluminum test dollys (0.5 cm²) were glued to the coated surface with a two-part Araldite 2015 adhesive glue and allowed to cure for 48 h at room temperature. Elcometer 108 adhesion of maximum applied load of 20 MPa tester was used. The pull-off strength loss values were calculated by the equation:

\[ \text{The pull−off strength \% loss} = \frac{a - b}{a} \times 100\% \]  

where \( a \) and \( b \) are dry pull-off strength and wet pull-off strength (7 days of immersion in 3.5% NaCl solution) respectively. All measurements were done in triplicate.

2.5. Water Contact Angle and Absorption Testing

Coating’s hydrophobicity was investigated by water contact angle (WCA) test using an OCA 15 EC (DataPhysics Instruments GmbH, Filderstadt, Germany) according to ASTM D7490 [30]. Droplets of water of 0.2 mL were carefully dispensed on the surface of the samples. The obtained WCA was evaluated on an average of 10 measurements taken on different points on the coating surface. Water absorption (\( Q_w \)) testing was conducted on epoxy and Gnps/epoxy coatings (thickness of 100 ± 10 µm). The formula below was used to determine the amount of water absorbed by the samples.

\[ Q_w = \frac{m_t - m_i}{m_i} \times 100\% \]  

where \( m_t \) and \( m_i \) are the mass of the coating before and after water absorption, respectively, and \( t \) representing the immersion time. Three parallel samples were used for all coating types for accurate evaluation. All coated samples were deeply immersed in distilled water without oxidation. Prior to measurement, samples were dried with a non-woven fabric to remove excess water on the surface. The mass of the coated samples was measured with a microbalance of 0.00001 g accuracy. The experiment was conducted over a 15-day period.

2.6. Salt Spray Testing

The corrosion properties of the Gnps/epoxy coatings were studied by salt spray testing. Coated samples 5 mm × 75 mm × 140 mm were put in a Q-FOG Cyclic Corrosion Tester (Q-Lab, Buckeye, AZ, USA). Prior to testing, the coated samples were X-cut 120 mm × 0.8 mm and exposed to 5% NaCl fog (pH of 6.5–7.2 and temperature of 35 °C) for 750 h according to ASTM B117 standards [31]. After testing, ISO 4628 –1:2016 standards [32] was used to assess coating’s performance.

2.7. Electrochemical Experiments

EIS measurements were performed using an Auto Lab PGSTAT302F (Metrohm, Switzerland) on a three-electrode cell, with coated steel specimen (1 cm² in area) as the working electrode, saturated calomel electrode (SCE) as reference electrode, and Pt electrode as counter electrode. The EIS was conducted for 28 days with a potential disturbance of ±20 mV within the frequency range of 0.01–10⁵ Hz at a rate of 10 points per decade and testing temperature was about 25 °C. The impedance data was processed with Nova 2.1 software (Version 2.1.4). To ensure reproducibility, three tests were performed under each condition.
3. Results

3.1. Characterization of Gnp/Epoxy Composite Coatings

Figure 2 shows the FE-SEM images of the three Gnp s under identical magnification. By observation, the shape morphology of all Gnp s were unidentical. C750 Gnp seemed lumpy and irregular with globe-like structure (Figure 2a). M15 Gnp showed a stacked structure with discontinuous scrambled surface made up of several spongy layers (Figure 2b) whereas X50 Gnp appeared as tiny uneven spherical particles entangled in an intertwined netlike structure (Figure 2c). However, the physical properties of the Gnp s matches with the reported data from the manufacturer mentioned in the experimental section. Moreover, the actual size distribution of the different Gnp s can easily be distinguished by their appearance in Figure 2.

![Figure 2](image_url)

**Figure 2.** SEM morphology of the Gnp s, (a–c): low magnification, (d–f) high magnification, (a,d) C750 Gnp, (b,e) M15 Gnp, (c,f) X50 Gnp.

Figure 3 demonstrates the FE-SEM images of the surface morphology of the prepared Gnp s/epoxy composite coatings and their EDS spectra. From the EDS spectra, elements such as C, O, Al, and Si were present in the Gnp s/epoxy coatings (Figure 3d). Specifically, the C and O elements depict the presence of graphene, whereas Si and Al are characteristic of epoxy which is consistence with [33]. It is clear that each coating possessed a peculiar dispersion morphology in the epoxy composite. For instance, C750 Gnp (Figure 3a) seemed homogeneously dispersed by exhibiting lesser agglomeration and aggregation. The homogenous dispersion can be attributed to the easy interaction with the epoxy matrix due to C750 Gnp s high surface area and smaller size [34,35]. Contrarily, M15 and X50 Gnp s (Figure 3b,c) were poorly dispersed with lots of agglomerates randomly formed. This is due to the poor interfacial interactions and weak intermolecular van der Waals forces between the Gnp s and the epoxy matrix [36]. The dispersion of Gnp s in epoxy coatings were also investigated at microscale using optical and stereoscopic microscopic images (in Figure 4). It is identified that, the C750 Gnp particles are greatly dispersed than the others (Figure 4a–c). For comparison, the Stereoscopic microscopic (SM) images obtained further confirmed a similar dispersion of Gnp s observed in the Optic microscopic (OM) images (Figure 4d–f).
3.2. Physical Properties of Gnps/Epoxy Composite Coatings

3.2.1. Adhesion Testing

Table 2 shows the adhesion results of neat epoxy and Gnps/epoxy coatings after 170 h immersion in 3.5% NaCl solution. All measurements were done in triplicate and
the average pull-off strength values were determined. It is discovered that the neat epoxy experienced a higher percentage loss of 37% but when Gnp s were added, the percentage loss reduced confirming an improved adhesion property of the epoxy coatings. Among the three Gnp s, C750 Gnp recorded the least percentage loss (9.6%) followed by M15 Gnp (14.6%) and X50 Gnp (19%) as shown in (Table 2). Moreover, Figure 5 demonstrated that the coating’s detachment from the surface of the bare steel was caused by the combination of adhesive and cohesive failures. The cohesive failure happens when the coatings adhesion bond to the steel surface is strong enough that the applied force overcomes the cohesive properties of the coating. On the other hand, when the interfacial adhesion bonds are not so strong the adhesion failure takes place. All prepared Gnps/epoxy coatings adhered much stronger to the substrate than the neat epoxy during both dry and wet testing, however, the overall adhesion loss percentage of C750 Gnp/epoxy coating was much improved as compared to M15 and X50 Gnp/epoxy coatings.

Table 2. Pull-off test results for Gnps/epoxy coatings after 7 days exposure to 3.5% NaCl solution.

| Coating Sample | Neat epoxy | C750 Gnp | M15 Gnp | X50 Gnp |
|----------------|------------|----------|---------|---------|
| Dry pull-off strength (MPa) | 5.99 | 9.42 | 6.78 | 6.90 |
| Wet Pull-off strength (MPa) | 3.77 | 8.51 | 5.79 | 5.54 |
| Pull-off strength % loss | 37% | 9.6% | 14.6% | 19% |

Figure 5. Optical images of epoxy and Gnps/epoxy composite coatings under dry and wet conditions of pull–off adhesion testing against of time.

3.2.2. Water Contact Angle Testing

Figure 6 shows the water contact angle values of the neat epoxy and Gnps/epoxy coatings. Generally, coating’s hydrophobic nature can be evaluated when the contact angle is determined. Coatings with contact angle less than 90°, greater than 90°, and above 90° are classified as hydrophilic, hydrophobic and super hydrophobic respectively. In this study, the contact angle value of the neat epoxy coating was 64° confirming epoxy’s hydrophilic nature. X50 Gnp/epoxy, M15 Gnp/epoxy and C750 Gnp/epoxy recorded contact angles of 72°, 81°, and 102° respectively indicating a significant change in the surface roughness of the neat epoxy after adding Gnp s. The rise in the contact angle can be linked to the hydrophobic properties of the different Gnp s which influenced the coatings tendency to reduce the amount of water uptake on the surface.
3.2.3. Water Absorption Testing

Figure 7 shows the time dependence of the percentage of water uptake of the neat epoxy and Gnp/epoxy coatings after 15 days of immersion. The graph obtained can be interpreted in three stages. Firstly, the curves followed a rapid linear growth, rose up slowly with increasing immersion days until equilibrium was attained at the final stage [37]. The other characteristic parameter is the maximum absorbed water content when saturation is reached. The result is summarized in Table 3 for all studied samples. Comparatively, the time and degree of saturation for the composite coatings were not the same. C750 Gnp/epoxy showed a minimum water absorption percentage of 0.85%, reaching equilibrium on the eighth day of immersion. For M15 Gnp/epoxy and X50 Gnp/epoxy coatings, the water absorption percentage of 0.94% and 1.21% were reached on the 10th and 11th day respectively. Neat epoxy reached equilibrium on the 13th day with 1.75% water absorption proving that the added Gnp's reduced water permeability of the coatings by reducing the free volume and restriction of the molecular dynamics of epoxy’s polymer chain segments as reported in previous study [38].

Table 3. Maximum absorbed water content % of neat epoxy, and Gnp/epoxy composite coatings when saturation was reached.

| Coating Samples | Neat epoxy | C750 Gnp | M15 Gnp | X50 Gnp |
|-----------------|------------|----------|---------|---------|
| Maximum absorbed water content % | 1.751 | 0.851 | 0.946 | 1.213 |
3.3. Corrosion Properties of Gnps/Epoxy Composite Coatings

3.3.1. Salt Spray Testing

Neat epoxy and Gnps/epoxy coated samples were exposed to a salt spray of 5% NaCl solution (based on ASTM B117) [31] for 750 h. Figure 8 shows the optical images against time. From the results, formation of flower-like disbonded area appeared around the scratched area for neat epoxy, X50 Gnp/epoxy and M15 Gnp/epoxy coatings after 48 h. It indicates the initiation of electrochemical reactions as corrosive ions diffused through the micro pores of neat epoxy matrix at the coating interface. Moreover, large blisters and brown-like discolored films were observed along the X scratched area which preceded to other parts of the surface of the neat epoxy coatings at the end of 750 h. The added Gnps showed an improved corrosion resistance at different testing times. For instance, rusting became serious after 300 h of testing for X50 Gnp/epoxy and after 480 h of testing for M15 Gnp/epoxy coatings. Meanwhile, C750 Gnp/epoxy coatings experienced mild rusting as few small blisters were observed around the X cut area after 750 h of testing. Further, there was no coating delamination proving that a strong interfacial bonding between C750 and the epoxy chains reduced brittleness, and hindered the diffusion of electrolyte. Table 4 shows the ranking of the coating failure after 750 h of salt spray testing according to ISO 4628–2 [32], which is used to assess the anti-corrosion performance of coatings. From the table, C750 Gnp/epoxy composite coatings showed an enhanced corrosion resistance compared to the M15, X50, and neat epoxy coatings.
Figure 8. Optical images of neat epoxy and GNPs/epoxy coatings under salt spray testing against immersion time.

Table 4. Ranking of coating failure after 800 h of salt spray testing according to ISO 4628–2 [39].

| Coating Sample       | Degree of Blistering | Degree of Blistering Size | Degree of Delamination |
|----------------------|----------------------|---------------------------|------------------------|
| Neat Epoxy           | 5                    | 5                         | Severe                 |
| C750 Gnp/epoxy       | 1                    | 1                         | Very Slight            |
| M15 Gnp/epoxy        | 2                    | 2                         | Slight                 |
| X50 Gnp/epoxy        | 3                    | 3                         | Considerable           |
3.3.2. EIS Characterization

EIS analysis was further employed to investigate the corrosion resistance of the nanocomposite coatings. Figure 9 illustrates the Bode and phase angle plots and its equivalent Nyquist diagram for the neat epoxy and Gnps/epoxy coatings in 3.5% NaCl solution. The curve appears as a one-time constant at the initial immersion stage and a two-time constant as penetration of corrosive media was initiated. The one-time constant is due to the capacitance impedance interaction with the coating interface that prevented corrosion process from taking place at the metal/coating interface. Generally, the low-frequency end impedance modules and the high-frequency end phase angles of the Bode plots decreased with increasing immersion time for all coated samples. It is evident that the Gnps/epoxy coatings demonstrated excellent corrosion performance compared to the neat epoxy that exhibited a clear degradation by recording the lowest impedance and phase angle values after total immersion days. However, C750 Gnp/epoxy coatings (Figure 9g,h) maintained a maximum phase angle and impedance change from the low to the high-frequency range compared to the M15 and X50 coating samples (Figure 9c–f). A minimum in the phase angle corresponds to a plateau in the impedance modulus [40]. Figure 10 shows the impedance values at the lowest frequency (i.e., |Z|0.01 Hz) of the coated samples. C750 Gnp/epoxy exhibited a small drop in impedance at |Z|0.01 Hz in the initial exposure times then increased after total immersion days. This was not witnessed in the other coatings where the drop values at |Z|0.01 Hz between exposure times decreased rapidly. In addition, two schematic Models A and B equivalent to electrical circuits (Figure 11) were employed to suit the EIS data. The Alternating current (AC) impedance was used to establish the coating’s capacitance and resistance to corrosion on the metallic substrate [41,42]. Model A represents a good corrosion resistance coating whiles Model B represents poor corrosion resistance coatings, where the model parameters are defined as follows: \( R_s \) is (solution resistance), \( \text{CPE}_{\text{ct}} \) is (Constant Phase Element) of the coating, \( R_c \) is the (coating resistance), \( \text{CPE}_{\text{dl}} \) is (Constant Phase Element) of the double-charge layer and \( R_d \) is (Charge transfer resistance) parameter [43]. The Bode plots of the neat epoxy compared to the Gnps/epoxy composite coatings (Figure 9) confirms the enhancing impact of Gnps in epoxy composites. Model A from the schematics corresponds with C750 Gnp/epoxy coating’s EIS results illustrated in (Figure 9g,h) whilst Model B corresponds to M15 Gnp/epoxy, X50 Gnp/epoxy, and neat epoxy coatings EIS results (Figure 9a–f). This implies C750 Gnp offered an effective barrier protection hence enhanced the surface barrier performance of the composite coatings than the other Gnps.

![Figure 9. Cont.](image-url)
Figure 9. Cont.
Figure 9. Bode plots of (a,b) neat epoxy, (c,d) X50 Gnp/epoxy, (e,f) M15 Gnp/epoxy, and (g,h) C750 Gnp/epoxy and Nyquist diagram of (i) neat epoxy, (j) X50 Gnp/epoxy, (k) M15 Gnp/epoxy, (l) C750 Gnp/epoxy coatings immersed in 3.5% NaCl solution for different exposure time.
Figure 10. Impedance values at low Frequency end (10 mHz) of prepared Gnp/epoxy composite coatings immersed in 3.5% NaCl solution at different Time.

All those was confirmed by the water uptake results (Figure 7). Conjointly, smaller size Gnps (M15 and X50) occupied a smaller domain in the epoxy matrix due to uneven dispersion and fewer agglomeration in contrast to the other composites. This phenomenon observed could be caused by their intrinsic size difference. Comparatively, the larger size Gnps (C750) are well-dispersed within the composites and provide more effective pathway to prevent diffusion of the corrosive agent. This extends the time taken for the corrosive agent to reach the metal substrate therefore providing a long-term anti corrosion protection. As confirmed in Figure 3, C750 Gnp of a smaller particle size experienced a better dispersion and fewer agglomeration in contrast to the other composites. This phenomenon observed could be caused by their intrinsic size difference. Comparatively, the larger size Gnps (M15 and X50) occupied a smaller domain in the epoxy matrix due to uneven dispersion that led to the formation of several aggregates in the composites, hence, offered a shorter route for the corrosion medium to reach the substrate under the same loading of Gnp weight. Homogeneous dispersion also enhances coatings absorption strength by reducing the amount of water molecules that penetrates into the coatings surface causing weaker links beneath the coatings thus decrease the coatings physical barrier qualities [44]. All those was confirmed by the water uptake results (Figure 7). Conjointly, smaller size Gnps

Figure 11. Equivalent electrical models used for EIS data.

4. Discussion

4.1. Morphological Influence on the Corrosion Properties of Gnp/Epoxy Composite Coatings

The surface barrier protection and corrosion properties of the composite coatings in this study was principally influenced by two morphological features (particle size and specific surface area). Figure 12 depicts a schematic mechanism for the size effect of Gnps on the anti-corrosion performance of the Gnp/epoxy coatings. It is clear that, smaller Gnps (C750) are well-dispersed within the composites and provide more effective pathway to prevent diffusion of the corrosive agent. This extends the time taken for the corrosive agent to reach the metal substrate therefore providing a long-term anti corrosion protection. As confirmed in Figure 3, C750 Gnp of a smaller particle size experienced a better dispersion and fewer agglomeration in contrast to the other composites. This phenomenon observed could be caused by their intrinsic size difference. Comparatively, the larger size Gnps (M15 and X50) occupied a smaller domain in the epoxy matrix due to uneven dispersion that led to the formation of several aggregates in the composites, hence, offered a shorter route for the corrosion medium to reach the substrate under the same loading of Gnp weight. Homogeneous dispersion also enhances coatings absorption strength by reducing the amount of water molecules that penetrates into the coatings surface causing weaker links beneath the coatings thus decrease the coatings physical barrier qualities [44]. All those was confirmed by the water uptake results (Figure 7). Conjointly, smaller size Gnps
do not only improve dispersion but also offers a high surface area which creates an efficient filler pathway to suppress corrosive attacks [33]. It is suggested that incorporation of a highly compatible nanoparticles of smaller particle size and high surface area improved the anti-corrosion performance of the coatings. This was in a good agreement with other reported studies [5,26,45].

![Figure 12. Schematic mechanism for enhanced anti-corrosion resistance of Gnps/epoxy composite coatings.](image)

**4.2. Mechanism for Enhanced Anti-Corrosion Resistance of Gnps/Epoxy Composite Coatings**

Significant study of Gnps corrosion protection mechanism can be classified as follows: (i) the compatibility of Gnps with epoxy helps reduce the interface defects in the coatings, (ii) the high surface energy owing to nanomaterials system creates a highly hydrophobic nanocomposite coating surface, (iii) Gnps improve the bonding strength at the coating–metal interface, and (iv) the impermeable nature of Gnps construct an excellent surface barrier against corrosive media by suppressing electrolyte pathways from the coating’s surface to prolong corrosion occurrence [5,12]. A similar anti-corrosion mechanism trend was observed in our study as an improved anti-corrosion performance was exhibited by the coatings incorporated with Gnps compared to the neat epoxy coatings (Figure 12). Generally, addition of the three Gnps reduced the interfacial defects in the epoxy matrix by effectively filling the micro-pores and cracks formed during curing thereby reducing the water absorption of the coatings (Figure 8). Moreover, the Gnps improved the surface hydrophobicity (Figure 6) and interfacial bonding force resulting in high adhesion strength (Figure 5). Poor adhesion permits aggressive ions to accumulate at the coating/metal interface that leads to corrosion [43]. In addition, the Gnps/epoxy composite coatings exhibited a physical shielding effect as witnessed in the salt spray test results (Figure 8). The EIS study further demonstrated a higher resistance for the Gnps/epoxy coatings (Figure 9) by generating an impediment towards the ionic electrolyte, which enhanced the corrosion protection capability of the coatings. However, among all the Gnps/epoxy composite coatings, C750 Gnp/epoxy exhibited the most effective physical surface barrier performance which can be employed in corrosion protection fields whereas the other Gnps had a little contribution to the corrosion resistance of the composite coatings. The enhanced anti-corrosion mechanism observed by the C750 Gnps can be accredited to the homogeneous dispersion that promoted a less formation of agglomerates [46,47].

5. Conclusions

Three different types of commercial Gnps incorporated into epoxy matrix were evaluated for their capabilities as enhanced barrier protection coatings. The coating’s overall performance, which consists of adhesion strength, hydrophobic nature, water absorption resistance and electrochemical properties were studied. The morphological impact of
the Gnps on the anti-corrosion performance was specifically investigated with precise conclusions as highlighted below:

- C750 Gnp of a smaller particle size and higher average surface area were highly favorable to initiate an efficient pathway that strongly suppressed the deeper penetration of corrosive agents. On the contrary, when agglomeration occurred due to difficult dispersion caused by larger size Gnps (X50 and M15), the nanoparticles were unable to fill the micro pores and voids in the epoxy composites thus caused the coating’s poor corrosion properties.

- The Gnps provided an excellent anti-corrosion mechanism by means of forming a passive protecting layer on the coating’s interface that hindered with the diffusion rate of corrosive media like O₂, H₂O, H⁺, and Cl⁻. However, the increased corrosion resistance of the Gnps/epoxy composite is attributed to the improved surface barrier’s influence on the coating’s anti-corrosion resistance and water uptake performance.

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**References**

1. Ibrahim, M.; Kannan, K.; Parangusan, H.; Eldeib, S.; Shehata, O.; Ismail, M.; Zarandah, R.; Sasadivuni, K.K. Enhanced corrosion protection of epoxy/ZnO-NiO nanocomposite coatings on steel. *Coatings* 2020, 10, 783. [CrossRef]

2. Xavier, J.R. Investigation on the anticorrosion, adhesion and mechanical performance of epoxy nanocomposite coatings containing epoxy-silane treated nano-MoO₃ on mild steel. *J. Adhes. Sci. Technol.* 2020, 34, 115–134. [CrossRef]

3. Zhou, X.; Huang, H.; Zhu, R.; Chen, R.; Sheng, X.; Xie, D.; Mei, Y. Green modification of graphene oxide with phytic acid and its application in anticorrosive water-borne epoxy coatings. *Prog. Org. Coat.* 2020, 143. [CrossRef]

4. Ammar, S.; Ramesh, K.; Ma, I.; Farah, Z.; Vengadaesvaran, B.; Ramesh, S.; Arof, A.K. Studies on SiO₂-hybrid polymeric nanocomposite coatings with superior corrosion protection and hydrophobicity. *Surf. Coat. Technol.* 2017, 324, 536–545. [CrossRef]

5. Ramezanzadeh, B.; Haeri, Z.; Ramezanzadeh, M. A facile route of making silica nanoparticles-covered graphene oxide nanohybrids (SiO₂-GO); fabrication of SiO₂-GO/epoxy composite coating with superior barrier and corrosion protection performance. *Chem. Eng. J.* 2016, 303, 511–528. [CrossRef]

6. Golru, S.S.; Attar, M.M.; Ramezanzadeh, B. Studying the influence of nano-Al₂O₃ particles on the corrosion performance and hydrolytic degradation resistance of an epoxy/polyamide coating on AA-1050. *Prog. Org.* 2014, 77, 1391–1399. [CrossRef]

7. Işın, D.; Kayaman-Apohan, N.; Güngör, A. Preparation and characterization of UV-curable epoxy/silica nanocomposite coatings. *Prog. Org.* 2009, 65, 477–483. [CrossRef]

8. Ammar, S.; Cheng, C.H.; Ma, I.A.W.; Baig, S.B.; Kasi, R.; Subramaniam, R.; Balakrishnan, V. Effects of TiO₂ nanoparticles on the overall performance and corrosion protection ability of neat epoxy and PDMS modified epoxy coating systems. *Front. Mater.* 2020, 6, 336. [CrossRef]

9. Ramezanzadeh, B.; Attar, M. Studying the corrosion resistance and hydrolytic degradation of an epoxy coating containing ZnO nanoparticles. *Mater. Chem. Phys.* 2011, 13, 1208–1219. [CrossRef]

10. Dhoke, S.K.; Khanna, A.S. Effect of nano-Fe₃O₃ particles on the corrosion behavior of alkyd based waterborne coatings. *Corros. Sci.* 2009, 51, 6–20. [CrossRef]

11. Shi, H.; Liu, F.; Yang, L.; Han, E. Characterization of protective performance of epoxy reinforced with nanometer-sized TiO₂ and SiO₂. *Prog. Org. Coat.* 2008, 62, 359–368. [CrossRef]

12. Liu, D.; Zhao, W.; Liu, S.; Cen, Q.; Xue, Q. Comparative tribological and corrosion resistance properties of epoxy composite coatings reinforced with functionalized fullerene C60 and graphene. *Surf. Coat. Technol.* 2016, 286, 354–364. [CrossRef]
13. Kumar, C.M.P.; Venkatesha, T.V.; Shabadi, R. Preparation and corrosion behavior of Ni and Ni–graphene composite coatings. Mater. Res. Bull. 2013, 48, 1477–1483. [CrossRef]

14. Pourhashem, S.; Vaeezi, M.R.A.; Bagherzadeh, M.R. Exploring corrosion protection properties of solvent based epoxy-graphene oxide nanocomposite coatings on mild steel. Corros. Sci. 2016, 115, 78–92. [CrossRef]

15. Ramanathan, T.; Abdala, A.A.; Stankovich, S.; Dikin, D.A.; Herrera-Alonso, M.; Piner, R.D.; Adamson, D.H.; Schniepp, H.C.; Chen, X.; Ruoff, R.S.; et al. Functionalized graphene sheets for polymer nanocomposites. Nat. Nanotechnol. 2008, 3, 327–331. [CrossRef]

16. Glover, C.F.; Richards, C.; Baker, J.; Williams, G.; McMurray, H.N. In-coating graphene nano-platelets for environmentally-friendly corrosion protection of iron. Corros. Sci. 2017, 114, 169–172. [CrossRef]

17. King, J.A.; Kliméz, D.R.; Miskioglu, I.; Odegard, G.M. Mechanical properties of graphene nanoplatelet/epoxy composites. J. Compos. Mater. 2014, 49, 659–668. [CrossRef]

18. Yadav, S.K.; Cho, J.W. Functionalized graphene nanoplatelets for enhanced mechanical and thermal properties of polyurethane nanocomposites. Appl. Surf. Sci. 2013, 266, 360–367. [CrossRef]

19. Kumar, A.M.; Khan, A.; Suleiman, R.; Qamar, M.; Saravanan, S.; Dafalla, H. Bifunctional CuO/TiO2 nanocomposite as nanofiller for improved corrosion resistance and antibacterial protection. Prog. Org. Coat. 2018, 114, 9–18. [CrossRef]

20. Frigione, M.; Lettieri, M. Recent advances and trends of nano-filled/nanostructured epoxies. Materials 2020, 13, 3415. [CrossRef]

21. Monetta, T.; Acquesta, A.; Bellucci, F. Graphene/epoxy coating as multifunctional material for aircraft structures. Aerospace 2015, 2, 423–434. [CrossRef]

22. Prolongo, S.G.; Jiménez-Suárez, A.; Moriche, R.; Ureña, A. Influence of thickness and lateral size of graphene nanoplatelets on water uptake in epoxy/graphene nanocomposites. Appl. Sci. 2018, 8, 1550. [CrossRef]

23. Kuo, W.-S.; Tai, N.-H.; Chang, T.-W. Deformation and fracture in graphene nanosheets. Coatings 2021, 11, 285. [CrossRef]

24. Liu, S.; Gu, L.; Zhao, H.; Chen, J.; Yu, H. Corrosion resistance of graphene-reinforced waterborne epoxy coatings. J. Mater. Sci. Technol. 2016, 32, 425–431. [CrossRef]

25. Starkova, O.; Buschhorn, S.T.; Mannov, E.; Schulte, K.; Anisikevich, A. Water transport in epoxy/MWCNT composites. Eur. Polym. J. 2013, 49, 2138–2148. [CrossRef]

26. Um, J.G.; Jun, Y.-S.; Alhumade, H.; Krithivasan, H.; Lui, G.; Yu, A. Investigation of the size effect of graphene nanoplatelets (GnPds) on the anti-corrosion performance of polyurethane/GnP composites. RSC Adv. 2018, 8, 17091–17100. [CrossRef]

27. Ziat, Y.; Hammi, M.; Zarhri, Z.; Laghlimi, C. Epoxy coating modified with graphene: A promising composite against corrosion behavior of copper surface in marine media. J. Alloys Compd. 2020, 820. [CrossRef]

28. Q235B Chinese GB Standard Equivalent, Properties, Specification and Composition. Available online: https://www.theworldmaterials.com/chinese-gb-standard/ (accessed on 28 February 2021).

29. ASTM D4541-17, Standard Test Method for Pull-off Strength of Coatings Using Portable Adhesion Testers; ASTM International: West Conshohocken, PA, USA, 2017.

30. ASTM D7490-13, Standard Test Method for Measurement of the Surface Tension of Solid Coatings, Substrates and Pigments using Contact Angle Measurements; ASTM International: West Conshohocken, PA, USA, 2017.

31. ASTM B117-19, Standard Practice for Operating Salt Spray (Fog) Apparatus; ASTM International: West Conshohocken, PA, USA, 2019.

32. ISO 4628-1:2016, Paints and Varnishes—Evaluation of Degradation of Coatings—Designation of Quantity and Size of Defects, and of Intensity of Uniform Changes in Appearance—Part 1: General Introduction and Designation System; International Organization for Standardization: Geneva, Switzerland, 2016.

33. ASTM D7490-13, Standard Test Method for Measurement of the Surface Tension of Solid Coatings, Substrates and Pigments using Contact Angle Measurements; ASTM International: West Conshohocken, PA, USA, 2017.

34. ASTM D4541-17, Standard Test Method for Pull-off Strength of Coatings Using Portable Adhesion Testers; ASTM International: West Conshohocken, PA, USA, 2017.

35. ASTM D4541-17, Standard Test Method for Pull-off Strength of Coatings Using Portable Adhesion Testers; ASTM International: West Conshohocken, PA, USA, 2017.

36. Schniepp, H.C.; Li, J.-L.; McAllister, M.J.; Sai, H.; Herrera-Alonso, M.; Prud’homme, R.K.; Car, R.; Saville, D.A.; Aksay, I.A. Functionalized single graphene sheets derived from splitting graphite oxide. J. Phys. Chem. B 2006, 110, 8535–8539. [CrossRef]

37. Chen, C.; Qiu, S.; Cui, M.; Qin, S.; Yan, G.; Zhao, H.; Wang, L.; Xue, Q. Achieving high performance corrosion and wear resistant epoxy coatings via incorporation of noncovalent functionalized graphene. Carbon 2017, 114, 356–366. [CrossRef]

38. Schniepp, H.C.; Li, J.-L.; McAllister, M.J.; Sai, H.; Herrera-Alonso, M.; Adamson, D.H.; Prud’homme, R.K.; Car, R.; Saville, D.A.; Aksay, I.A. Functionalized single graphene sheets derived from splitting graphite oxide. J. Phys. Chem. B 2006, 110, 8535–8539. [CrossRef]

39. Volovitch, P.; Vu, T.N.; Allély, C.; Abdel Aal, A.; Ogle, K. Understanding corrosion via corrosion product characterization: II. Role of alloying elements in improving the corrosion resistance of Zn–Al–Mg coatings on steel. Corros. Sci. 2011, 53, 2437–2445. [CrossRef]

40. Jüttner, K. Electrochemical impedance spectroscopy (EIS) of corrosion process on inhomogeneous surfaces. Electrochim. Acta 1990, 35, 1501–1508. [CrossRef]
41. Ghanbari, A.; Attar, M.M. A study on the anticorrosion performance of epoxy nanocomposite coatings containing epoxy-silane treated nano-silica on mild steel substrate. *J. Ind. Eng. Chem.* **2015**, *23*, 145–153. [CrossRef]
42. Wang, X.; Tang, F.; Qi, X.; Lin, Z. Mechanical, electrochemical, and durability behavior of graphene nano-platelet loaded epoxy-resin composite coatings. *Compos. B Eng.* **2019**, *176*. [CrossRef]
43. Parhizkar, N.; Ramezanzadeh, B.; Shahrabi, T. Corrosion protection and adhesion properties of the epoxy coating applied on the steel substrate pre-treated by a sol-gel based silane coating filled with amino and isocyanate silane functionalized graphene oxide nanosheets. *Appl. Surf. Sci.* **2018**, *439*, 45–59. [CrossRef]
44. Prolongo, S.G.; Gude, M.R.; Ureña, A. Water uptake of epoxy composites reinforced with carbon nanofillers. *Compos. Part A Appl. Sci. Manuf.* **2012**, *43*, 2169–2175. [CrossRef]
45. Qi, K.; Sun, Y.; Duan, H.; Guo, X. A corrosion-protective coating based on a solution-processable polymer-grafted graphene oxide nanocomposite. *Corros. Sci.* **2015**, *98*, 500–506. [CrossRef]
46. Dorri Moghadam, A.; Omran, E.; Menezes, P.L.; Rohatgi, P.K. Mechanical and tribological properties of self-lubricating metal matrix nanocomposites reinforced by carbon nanotubes (CNTs) and graphene—A review. *Compos. B Eng.* **2015**, *77*, 402–420. [CrossRef]
47. Montazeri, A.; Chitsazzadeh, M. Effect of sonication parameters on the mechanical properties of multi-walled carbon nanotube/epoxy composites. *Mater. Des.* **2014**, *56*, 500–508. [CrossRef]