

Article



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], Fe_2O_3 [10], TiO_2 [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, Monetta



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 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).

Table 1. Physical properties of commercialized Gnps used in this study.

Grade	Diameter (µm)	Specific Surface Area (m^2g^{-1})
C750 Gnp	<2	\sim 750
M15 Gnp	<15	${\sim}150$
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 $(H_2O:HCI: methacrylic acid)$ 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, brushcoated 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 \pm 20 μ m 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 $200 \times$ and $1000 \times$ (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

 $20,000 \times$ 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 dollies (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:

The pull – off strength % loss =
$$\frac{a-b}{a} \times 100\%$$
 (1)

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 $100 \pm 10 \mu m$). The formula below was used to determine the amount of water absorbed by the samples.

$$Q_w = \frac{m_t - m_i}{m_i} \times 100\%$$
⁽²⁾

where m_i 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 \times 75 mm \times 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 \times 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 $0.01-10^5$ 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 Gnps/Epoxy Composite Coatings

Figure 2 shows the FE-SEM images of the three Gnps under identical magnification. By observation, the shape morphology of all Gnps 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) whiles X50 Gnp appeared as tiny uneven spherical particles entangled in an intertwined netlike structure (Figure 2c). However, the physical properties of the Gnps matches with the reported data from the manufacturer mentioned in the experimental section. Moreover, the actual size distribution of the different Gnps can easily be distinguished by their appearance in Figure 2.



Figure 2. SEM morphology of the Gnps, (**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 Gnps/epoxy composite coatings and their EDS spectra. From the EDS spectra, elements such as C, O, Al, and Si were present in the Gnps/epoxy coatings (Figure 3d). Specifically, the C and O elements depict the presence of grapheme, 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 Gnps high surface area and smaller size [34,35]. Contrarily, M15 and X50 Gnps (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 Gnps and the epoxy matrix [36]. The dispersion of Gnps 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 Gnps observed in the Optic miscroscopic (OM) images (Figure 4d–f).



Figure 3. SEM images of the surface morphology of (**a**) C750 Gnp/epoxy, (**b**) M15 Gnp/epoxy, (**c**) X50 Gnp/epoxy coatings at low and high magnification as well as EDS spectra (**d**) measured at different points.



Figure 4. OM images of the dispersion morphology of (**a**) C750 Gnp/epoxy, (**b**) M15 Gnp/epoxy and (**c**) X50 Gnp/epoxy and SM images of (**d**) C750 Gnp/epoxy, (**e**) M15 Gnp/epoxy and (**f**) X50 Gnp/epoxy composite coatings.

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 Gnps were added, the percentage loss reduced confirming an improved adhesion property of the epoxy coatings. Among the three Gnps, 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 Gnps. The rise in the contact angle can be linked to the hydrophobic properties of the different Gnps which influenced the coatings tendency to reduce the amount of water uptake on the surface.



Figure 6. Surface contact angle of (a) neat epoxy, (b) X50 Gnp/epoxy, (c) M15 Gnp/epoxy, and (d) C750 Gnp/epoxy coatings.

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 Gnps 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 Gnps/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



Figure 7. Time dependence of the percentage of water absorption in neat epoxy resin and epoxy composites reinforced with C750, M15, and X50 Gnps.

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. Futher, 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.

Coatings	Ероху	C750	M15	X50
0 h		\mathbf{X}	\times	\times
48 h	X			X
96 h	X		X	X
300 h	X		X	X
520 h	X			
750 h	X			

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 lowfrequency 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), CPE_{po} is (Constant Phase Element) of the coating, R_c is the (coating resistance), CPE_{dl} is (Constant Phase Element) of the double-charge layer and R_{ct} 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.



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.



Figure 11. Equivalent electrical models used for EIS data.

4. Discussion

4.1. Morphological Influence on the Corrosion Properties of Gnps/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 Gnps/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.

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 coatingmetal 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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