The influence of graphene oxide functionalized with 3-aminopropyl triethoxysilane on the corrosion protection performance of epoxy coatings

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ABSTRACT

This study reports the synthesis and characterization of graphene oxide functionalized with 3-aminopropyl triethoxysilane (GO-APTES) to enhance its dispersion within an epoxy resin for advanced anticorrosion coating applications. The structural morphology of the material was characterized using Fourier-transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy (FE-SEM), and energy-dispersive X-ray spectroscopy (EDX). The anticorrosive performance of the GO-APTES/epoxy nanocomposite coating was evaluated using electrochemical impedance spectroscopy (EIS). The epoxy coating incorporating GO-APTES exhibited outstanding corrosion resistance, effectively protecting the metal substrate for up to 60 days of immersion in a 3.5% NaCl solution. The results indicate that the silane-functionalized graphene oxide not only achieves excellent dispersion within the epoxy matrix but also contributes to forming a compact and uniform barrier layer that significantly inhibits the diffusion of corrosive media into the substrate. In particular, the GO-APTES/EP coating demonstrated a high corrosion protection efficiency of 95.61% on CT3 steel, further confirming the remarkable barrier performance of the modified system.

Keywords: GO; APTES; Coating; Anticorrosive.

1. INTRODUCTION

Metallic materials, particularly iron and steel, are the backbone of modern industry, including transportation, energy, and high-tech manufacturing. During service, the structure and properties of these materials degrade significantly, primarily due to corrosion. With a coastline stretching over 3,200 kilometers and a consistently hot, humid tropical climate, Vietnam experiences an accelerated rate of corrosion, particularly in its coastal and marine infrastructure. Therefore, implementing effective corrosion protection strategies for steel-based structural materials is critically important not only to ensure the sustainable development of the national economy but also to make a meaningful contribution to environmental protection.

Among various methods for protecting metals against corrosion, surface coating is one of the most widely employed approaches due to its ability to isolate the metal substrate from aggressive environments by forming a barrier layer. These coatings are characterized by good adhesion, excellent corrosion resistance, high durability, ease of application, and relatively low cost. In recent years, numerous nanofillers have been incorporated into epoxy resin matrices to enhance the barrier and protective properties of anticorrosion coatings. Graphene oxide (GO) has attracted significant attention due to its ultrathin layered structure, exceptionally high surface area, and abundant oxygen-containing functional groups. The unique architecture of GO provides an effective physical barrier that slows the diffusion of corrosive agents such as water, oxygen, and chloride ions to the metal surface [1].

Despite its exceptional physicochemical properties, pristine graphene oxide (GO) exhibits certain limitations, particularly in terms of dispersion stability and interfacial compatibility with polymer matrices, which can adversely affect long-term corrosion protection performance. To overcome these drawbacks, surface functionalization of GO is considered an essential strategy to improve its dispersibility and enhance interfacial adhesion to metallic substrates. Among various coupling agents, 3-aminopropyltriethoxysilane (APTES) has proven to be a highly effective modifier [2]. It forms covalent bonds with oxygen-containing functional groups on GO. It introduces silanol groups capable of forming strong interactions with metal or metal oxide surfaces, enhancing coating stability and anticorrosion performance. Stable covalent linkages are formed through the reaction between the amine group ($–NH_2$) of APTES and the carboxyl or epoxy groups on GO, contributing to surface structure control and improved dispersion in organic solvents. Moreover, the triethoxysilane functional group can hydrolyze to generate silanol (–Si–OH) groups, which can strongly interact with the hydroxylated metal surface, thus significantly improving the interfacial adhesion and long-term stability of the protective coating. Incorporating APTES-functionalized GO (GO–APTES) into epoxy-based coatings has demonstrated improved corrosion resistance and holds great promise for extending the service life of metallic substrates under harsh environmental conditions.

This study presents a method for synthesizing 3-aminopropyltriethoxysilane-functionalized graphene oxide (GO–APTES) as a corrosion-inhibiting additive in epoxy coating systems. The corrosion inhibition performance of the modified material was evaluated using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques.

2. EXPERIMENT

2.1. Materials

- GO was synthesized according to a previously published procedure [3].
- 3-aminopropyl triethoxysilane (APTES), dibutyltin dilaurate, and N, N-dimethylformamide (DMF) were of analytical grade and purchased from Merck.
- Methyl isobutyl ketone (Macklin, China) was used as the solvent for paint formulation.
- Ethanol, methanol, and NaCl were of analytical grade and purchased from Macklin (China).
- Epoxy resin YD011-X75 (solid content: 75%) and the polyamide curing agent G700-X60 were supplied by Kukdo Chemical Co., Ltd. (South Korea).

Mild steel (CT3 grade) was used as the metal substrate for electrode fabrication and corrosion evaluation in this study. The steel surface and electrode samples were pretreated by sequential grinding using abrasive papers with increasing grit sizes: 180, 400, 1000, and 2000.

All chemicals were used as received without further purification.

2.2. Synthesis of 3-aminopropyl triethoxysilane functionalized graphene oxide (GO-APTES)

GO (2.5 g) was first dispersed in a mixed solvent system containing 25 mL of DMF and 25 mL of C_2H_5OH using an ultrasonic probe (1500 W) for 5 hours to ensure effective exfoliation and uniform dispersion. The resulting suspension was then subjected to high-speed homogenization for 3 hours. Subsequently, APTES was added to the dispersion at a concentration of 1 mL APTES per 1 g of GO, along with 500 mL of C_2H_5OH. To adjust the reaction medium to a mildly acidic pH of 4–5, a dilute acetic acid solution (0.1 M HCl) was added dropwise during stirring. A catalyst (0.5 g of dibutyltin dilaurate) was also added, and the mixture was stirred at 1000 rpm for 5 hours at 75 ºC. After the reaction was completed, the product was washed with C_2H_5OH and centrifuged to remove residual catalyst and unreacted silane. The final product was vacuum-dried at 60 ºC for 12 hours to obtain the 3-aminopropyl triethoxysilane-functionalized graphene oxide material, denoted as GO-APTES.

2.3. Preparation of GO-APTES/epoxy coating

The powder GO-APTES 2%wt. was first dispersed in methyl isobutyl ketone to form a homogeneous solution. An appropriate amount of epoxy resin (EP) was then added and mixed at high speed to obtain a uniform dispersion of GO-APTES/EP. A polyamide curing agent was subsequently added to the mixture, which was vigorously stirred to ensure thorough homogenization. The resulting coating mixture was passed through a fine mesh to eliminate air bubbles before application.

In this study, mild steel plates (CT3 grade) with dimensions of 70 × 100 × 1 mm were used as substrates. The steel specimens were degreased with soap solution, wiped, and dried. Surface rust was removed using a wire brush and polishing with 400-grit sandpaper. The cleaned samples were then rinsed with distilled water and absolute ethanol and dried.

The GO-APTES/EP coating was applied to the pretreated steel substrates using a spray coating method. After drying, the resulting film was approximately 50 ± 5 µm thick, measured using an Ecometer thickness gauge. An unmodified epoxy coating (without GO-APTES) was prepared under identical conditions and used as a control sample.

2.4. Materials characterization and properties

Characterization

An energy-dispersive X-ray (EDX) spectrometer was attached to the FE-SEM instrument. Fourier transform infrared (FT-IR) spectra were recorded by an FT-IR NEXUS 670 spectrometer with wave numbers from 400 to 4000 cm^{-1}.

Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) and Potentiodynamic polarization (Tafel) were conducted on coated steel samples covered with the GO-APTES/EP film. A PVC tube containing 50 mL of 3.5% NaCl solution was affixed to the surface of the coated specimen, exposing a working area of 16 cm^2. The impedance spectra were recorded after immersion periods of 7, 30, and 60 days. Measurements were carried out in the frequency range from 100 kHz to 10 mHz using an automatic scan mode. A control sample coated with pure epoxy was also tested under the same conditions for comparison. All electrochemical measurements were performed using an AUTOLAB PGSTAT 302N workstation at the Institute of Chemistry and Materials. Each electrochemical test was repeated three times to ensure the reliability of the experimental data.

Adhesion test

The coating adhesion was evaluated using the cross-cut method by ASTM D3359. After curing, the coating surface was incised into a lattice pattern using a specialized cutter, followed by the application and removal of standardized adhesive tape. Adhesion was rated on a scale from 0 to 5, where 0 indicates excellent adhesion (no peeling) and 5 represents complete coating detachment.

3. RESULTS AND DISCUSSION

3.1. Characterization

FT-IR spectra

The interaction between GO and APTES was investigated by FT-IR spectroscopy. The result is presented in figure 1. As observed in Figure 1, a broad absorption band at 3440 cm^1 corresponds to the O–H stretching vibrations of hydroxyl groups on the GO surface and the N–H stretching from the introduced amine functionalities. A peak at 2900 cm^{-1} is attributed to the C–H stretching vibrations of aliphatic –CH$_2$ groups, indicating the presence of alkyl chains introduced by the silane modifier (APTES). The peak at 1630 cm^{-1} is related to the C=C skeletal vibrations of the aromatic carbon framework. In addition, an absorption band at 1042 cm^{-1} is observed, corresponding to the asymmetric stretching of Si–O–Si bonds, which confirms the successful condensation and grafting of silane molecules onto the GO surface. Furthermore, the small band around 680 cm^{-1} is associated with the bending vibrations of Si–C bonds, providing additional evidence of covalent bond formation between GO and APTES. These results confirm the successful functionalization of GO with the organosilane compound, which agrees with previous literature reports [4].

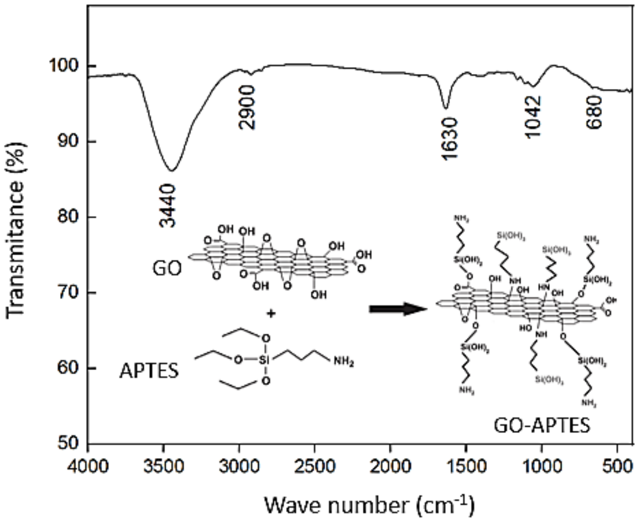

***Figure 1.** FT-IR spectra of GO-APTES material.*

FE-SEM image and EDX spectra

The surface morphology of the GO-APTES material was examined by field emission scanning electron microscopy (FE-SEM). The results in Figure 2A show that the GO-APTES exhibits a layered, wrinkled structure with roughened and uneven surfaces. The characteristic thin, sheet-like morphology of graphene oxide is retained; however, the edges appear more crumpled, and the surfaces become less smooth after silanization. This change is attributed to the successful grafting of APTES molecules onto the GO surface, which increases the interlayer spacing between adjacent GO sheets. The presence of rough and partial folding indicates an increased density of functional groups, which enhances interfacial interactions with polymer matrices, such as epoxy.

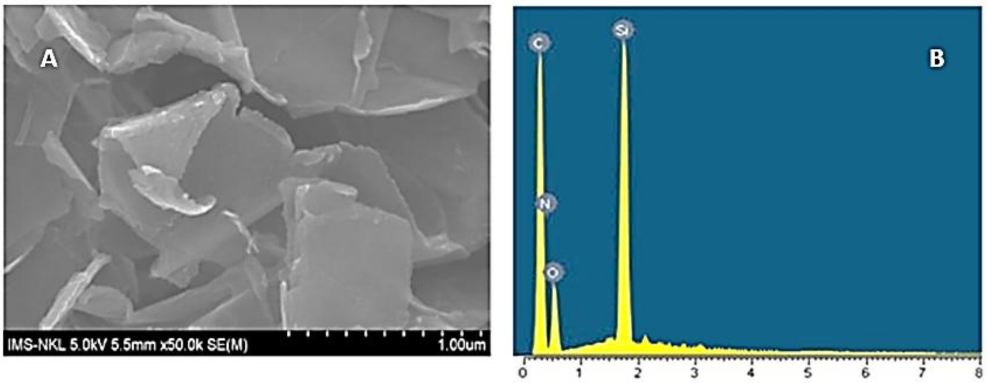

***Figure 2.** (A) FE-SEM image and (B) EDX spectra of GO-APTES material.*

Energy-dispersive X-ray spectroscopy (EDX) was employed to determine the elemental composition of the synthesized material, as shown in Figure 2B. The EDX spectrum confirms the presence of C and O as the significant elements, with characteristic peaks appearing at 0.27 keV and 0.52 keV, respectively. These are consistent with the graphitic carbon framework and oxygen-containing functional groups of graphene oxide. The detection of a distinct peak at 0.39 keV corresponds to N, indicating the successful introduction of amine functionalities from the APTES molecules. In addition, a strong peak at around 1.74 keV is attributed to Si, further confirming silane grafting onto the GO surface via Si–O–C or Si–Si linkages.

The corresponding EDX elemental mapping images for C, O, Si, and N demonstrate a uniform distribution of these elements across the observed region. The homogeneous dispersion of Si and N suggests that the APTES molecules are evenly attached to the GO sheets. This uniform functionalization is essential for enhancing the dispersion of GO in polymer matrices and promoting adequate interfacial bonding in composite systems.

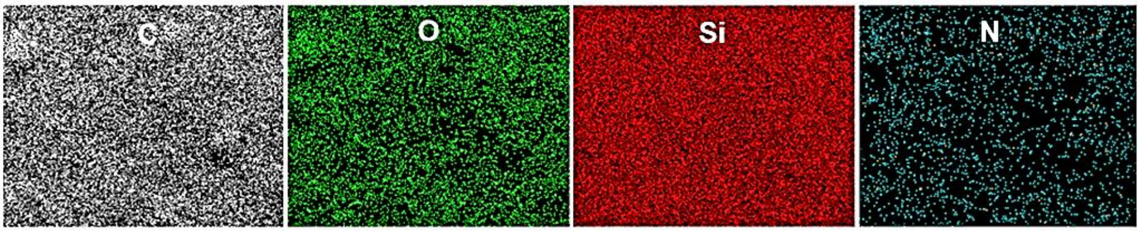

Figure 3. *EXD mapping spectra of the GO-APTES material.*

The weight and atomic percentages of the elements present in GO-APTES were determined by EDX analysis and averaged over five different locations. The results are summarized in Table 1.

Table 1. *Elemental composition of GO-APTES.*

Sample	Element	Weight (%)	Atomic (%)
GO-APTES	C	59.64	68.13
	N	6.25	6.48
	O	24.25	20.62
	Si	9.86	4.77

As shown in table 1, the GO-APTES material predominantly consists of C (~59%) and O (~24%), characteristic of the graphene oxide framework. Additionally, the presence of N (~6%) and Si (~10%) indicates the successful incorporation of APTES onto the GO surface. The detection of nitrogen confirms the presence of amine groups introduced by APTES. At the same time, the silicon content is consistent with the grafting of the silane moiety, providing further evidence of effective surface functionalization. This elemental composition not only confirms the successful surface modification of GO but also suggests that the introduced functional groups can play a crucial role in enhancing interfacial interactions and facilitating the uniform dispersion of GO-APTES within epoxy matrices for advanced coating applications.

3.2. Corrosion resistance analysis

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a reliable technique for evaluating the protective performance of organic coatings. Generally, the higher impedance values indicate better barrier properties. A coating is considered highly protective when its resistance exceeds 10^9 Ω.cm^2, while values below 10^6 Ω.cm^2 indicate loss of corrosion protection [5]. The corrosion resistance of the GO-APTES/EP coating was evaluated using EIS in a 3.5% NaCl solution after 7, 30, and 60 days of immersion, with pure epoxy (EP) used as a reference.

As illustrated in Figure 4, the impedance spectra undergo significant changes with increasing immersion time. The EIS data of the EP coating (figure 5A) reveal two well-defined capacitive loops. The high-frequency semicircle is attributed to the intrinsic barrier properties of the coating, whereas the low-frequency semicircle is associated with electrochemical reactions at the coating–substrate interface. After prolonged immersion, the EP coating exhibited a total impedance of 1.53 × 10^5 Ω.cm^2, suggesting a decline in its protective performance and indicating the beginning of corrosion processes at the steel surface.

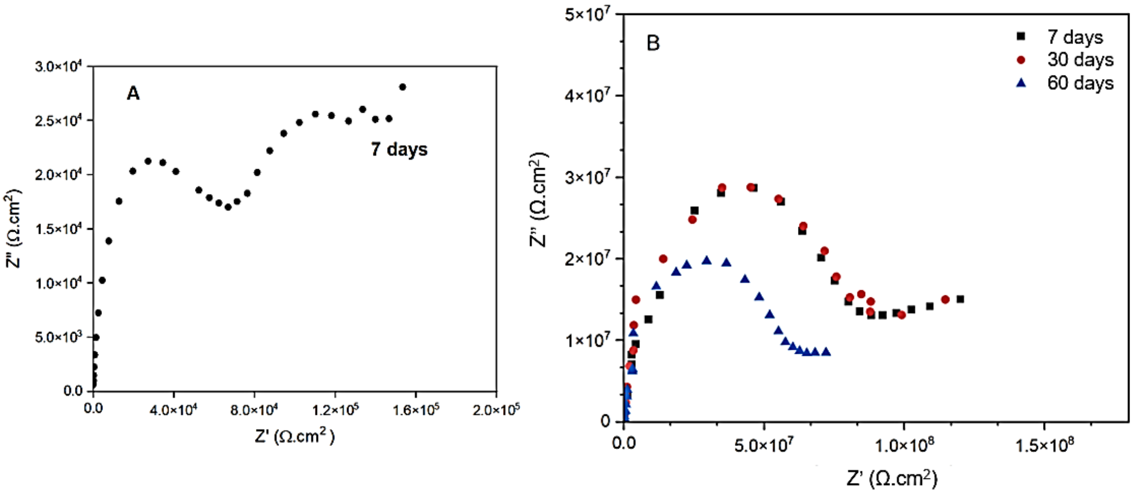

Figure 5. *EIS data of (A) EP coating and (B) GO-APTES/EP coating in 3.5 wt% NaCl solution.*

Figure 5B shows that after 7 days of immersion, the GO-APTES/EP coating exhibits a high-frequency capacitive semicircle with the initial emergence of a low-frequency tail, indicating partial electrolyte penetration. The total impedance value at 0.01 Hz, reached 1.25 × 10^8 Ω.cm², is approximately three times higher than the EP coating. This significant enhancement reflects the superior barrier properties of silane-functionalized graphene oxide. The APTES molecules not only improve the dispersion of GO in the epoxy matrix but also promote strong interfacial interactions through the formation of covalent bonds with the epoxy resin and hydrogen bonding on the metal substrate [5].

After 30 days, a slight decrease in the semicircle diameter is observed, indicating gradual electrolyte ingress; however, the impedance remains approximately 10^8 Ω.cm². After 60 days, the coating still exhibited a single capacitive loop with a small low-frequency tail, and the impedance remained on the order of 7.5 × 10^7 Ω.cm², indicating minimal degradation and sustained corrosion resistance.

These results confirm that GO-APTES/EP provides stable long-term anticorrosion protection through the synergistic effects of the GO nanosheet barrier and APTES-induced interfacial reinforcement. The evolution of low-frequency impedance (Z_{10} mHz), a key indicator of coating degradation, is shown in figure 6A.

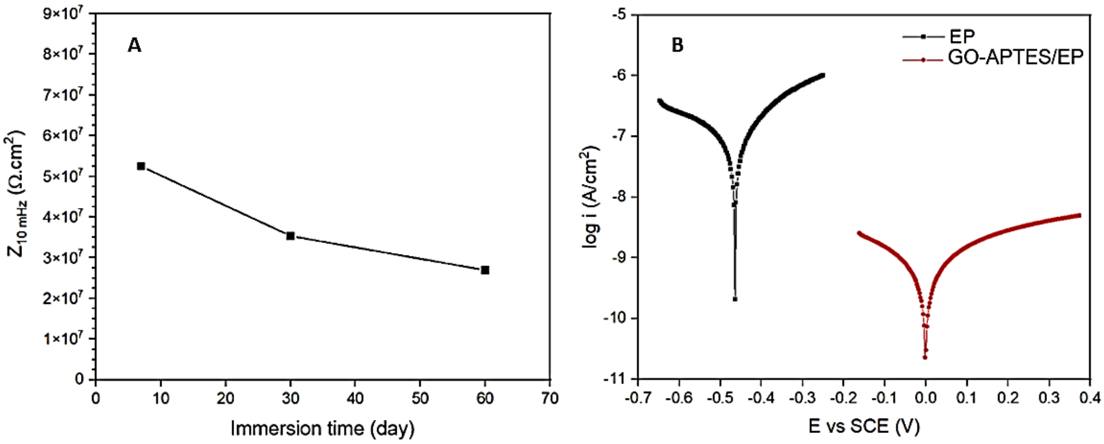

Figure 6. *(A) The Z_{10} mHz values of the coatings and (B)The Tafel polarization curves of the coatings on CT3 steel after 60 days of immersion in 3.5 wt% NaCl solution.*

The results shown in figure 6A indicate that the impedance modulus at low frequency (Z_{10} mHz) decreased after immersion in the electrolyte solution. After 60 days of exposure, the Z_{10} mHz values remained on the order of ~10^7 Ω.cm^2 for all coatings, suggesting they still provided adequate corrosion protection. The functionalization of graphene oxide with APTES plays a critical role in enhancing interfacial adhesion and impeding electrolyte ingress, thereby extending the service life of the protective coating under saline conditions.

Potentiodynamic polarization

The corrosion-protection performance of the GO-modified APTES/epoxy (GO–APTES/EP) coating was further evaluated using potentiodynamic polarization measurements. The polarization curves of the GO–APTES/EP coating applied on CT3 steel after 60 days of immersion in 3.5 wt% NaCl solution are presented in Figure 6B. A pure epoxy (EP) coating was also tested as a reference. The electrochemical parameters extrapolated from the polarization curves, including the corrosion potential (E_{corr}) and corrosion current density (i_{corr}), are summarized in Table 2.

Table 2. *Electrochemical parameters of coatings after 60 days in 3.5 wt% NaCl.*

Materials	***E_{corr} (mV)***	***i_{corr} (nA/cm^2)***
EP	- 463	10,26
GO-APTES/EP	- 23	0,45

Compared with the uncoated steel, the polarization curve of the GO-APTES/EP coating is shifted toward lower current densities and more positive potentials. The corrosion potential of the EP coating on CT3 steel after 60 days of immersion was measured at –463 mV. In contrast, the EP coatings incorporating GO–APTES exhibited more positive corrosion potentials of –23 mV, respectively. According to Leidhiser et al., a shift of E_{corr} toward the anodic direction indicates suppression of the anodic reaction. This observation suggests that the functionalized GO dispersed within the epoxy matrix provides an effective barrier and inhibitory effect, thereby increasing the corrosion potential of the coated steel surface [6].

The measured corrosion current density of the EP coating containing APTES-functionalized GO was 0.45 nA/cm^2, which is significantly lower than that of the neat epoxy coating (10.26 nA/cm^2). This reduction in current density is attributed to the uniform dispersion of GO–APTES within the epoxy matrix, forming a compact and continuous barrier layer that shields the steel surface and prevents electrochemical interaction between the NaCl solution and the substrate. Consequently, the corrosion potential increases, the corrosion current is suppressed, and the overall corrosion rate is markedly reduced.

Additionally, the excellent dispersion of GO-APTES contributes to a denser microstructure within the coating. As evidenced by the FE-SEM cross-section image (Figure 7), the GO-APTES/EP coating exhibits a highly uniform and compact morphology without visible voids or interfacial defects. This homogeneous internal structure indicates that GO-APTES nanosheets are well-distributed throughout the epoxy network, creating a more tortuous diffusion pathway that effectively retards the penetration of corrosive species such as Cl^- ions and moisture. Such morphology strongly correlates with the observed reduction in icorr and confirms the role of APTES functionalization in enhancing the structural integrity and barrier performance of the coating.

The corrosion protection efficiency of the functionalized GO/EP coating on CT3 steel in NaCl solution was determined using the following equation:

$$H = \frac{i^o corr - i\ corr}{i\ corr}\ x\ 100\% \qquad (1)$$

Whereas:

$i^o{}_{corr}$ is the corrosion current density of the EP coating in 3.5 wt% NaCl solution.

i_{corr} is the corrosion current density of the GO-APTES/EP coating in 3.5 wt% NaCl solution.

From Equation (1), the corrosion protection efficiency of GO-APTES/EP for CT3 steel was calculated to be 95.61%.

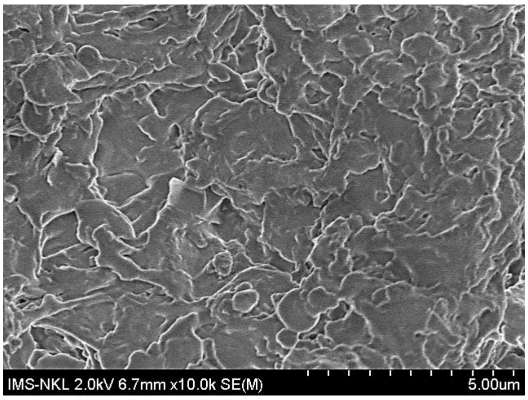

***Figure 7.** FE-SEM cross-section image of the GO-APTES/EP coating.*

The FE-SEM results and electrochemical data demonstrate that the improved dispersion and strong interfacial bonding imparted by APTES are key factors enabling the high anticorrosion efficiency of the GO-APTES/EP coating system. This result is consistent with several reports [7, 8], which also demonstrated that the use of amino-functionalized GO significantly enhances the anticorrosion performance of epoxy coatings.

3.3. Adhesion test results

The adhesion strength was determined using the pull-off test method by the ASTM D 3359 standard. Adhesion test results revealed that the pure EP coating received a rating of 1, whereas the GO–APTES/EP coating achieved a superior rating of 0, based on the standard adhesion scale. This significant improvement indicates that the incorporation of GO-APTES greatly enhances the interfacial bonding between the coating and the metal substrate. The silanol groups in APTES can form chemical bonds with hydroxyl groups, also interacting favorably with the epoxy matrix. As a result, the GO-APTES/EP coating exhibits a more stable interphase structure, reducing film separation under corrosive environmental conditions. This observation is consistent with the impedance data and confirms the beneficial role of silane modification in improving the overall protective performance of the coating system.

4. CONCLUSIONS

In this study, epoxy-based coatings incorporating 3-aminopropyl triethoxysilane-functionalized graphene oxide were successfully fabricated and evaluated for their anticorrosion performance in a 3.5 wt.% NaCl solution. After 60 days of immersion in 3.5 wt.% NaCl solution, the coating still provided adequate corrosion protection with a coating resistance of 10^7 Ω.cm^2. Furthermore, the GO-APTES/EP coating achieved a high corrosion protection efficiency of 95.61%, demonstrating its superior ability to inhibit the penetration of corrosive species. Overall, the results confirm that silane functionalization of GO significantly enhances the anticorrosion efficiency and interfacial stability of epoxy coatings, offering a promising strategy for long-term protection of metal substrates in aggressive environments.

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TÓM TẮT

Ảnh hưởng của graphene oxit biến tính bằng 3-aminopropyl triethoxysilane đến khả năng bảo vệ chống ăn mòn của lớp phủ epoxy

Bài báo này trình bày phương pháp tổng hợp vật liệu graphen oxit biến tính 3-aminopropyl triethoxysilane (GO-APTES) phân tán trong nhựa epoxy ứng dụng bảo vệ chống ăn mòn kim loại. Hình thái cấu trúc của vật liệu được đánh giá bằng phương pháp phổ hồng ngoại (FT-IR), kính hiển vi điện tử quét phát xạ trường (FE-SEM),), phổ tán sắc năng lượng tia X (EDX). Khả năng bảo vệ chống ăn mòn của vật liệu được đánh giá bằng phổ tổng trở điện hóa. Màng phủ epoxy chứa GO-APTES có khả năng bảo vệ kim loại đến 60 ngày ngâm trong dung dịch NaCl 3,5%. Kết quả nghiên cứu cho thấy GO-APTES có khả năng phân tán tốt trong nhựa epoxy, tạo lớp màng bảo vệ ngăn chặn sự xâm nhập của môi trường ăn mòn. Hiệu suất bảo vệ chống ăn mòn của màng GO-APTES/EP trên nền thép CT3 đạt 95,61%.

Từ khoá: GO; APTES; Lớp phủ; Bảo vệ chống ăn mòn.