Study on the effect of halloysite nanotubes on the adhesion and corrosion protection of epoxy coatings on carbon steel

Tran Van Cuong[1], Dinh Tran Kim Nguyen[2], Nguyen Nhi Tru[2], Pham Thanh Hai[1*]

[1]Institute for Tropical Technology, Academy of Military Science and Technology, 57A Truong Quoc Dung, Phu Nhuan, Ho Chi Minh City, Vietnam;
[2]Ho Chi Minh University of Technology – Vietnam National University Ho Chi Minh City, 268 Ly Thuong Kiet, Dien Hong, Ho Chi Minh City, Vietnam.
[*]Corresponding author: thanhhaipham@vittep.com
Received 15 Aug. 2025; Revised 2 Oct. 2025; Accepted 16 Oct. 2025; Published 18 Nov. 2025.
DOI: https://doi.org/10.54939/1859-1043.j.mst.IMBE.2025.179-185

ABSTRACT

Halloysite nanotubes (HNT) are naturally occurring clay minerals with abundant reserves, commonly employed as carriers for corrosion inhibitors in protective coatings. However, the direct influence of HNT on the physico-mechanical properties and corrosion resistance of coatings has received limited attention. In this study, a procedure for dispersing HNT into an epoxy binder was established, and the effect of HNT loading on adhesion strength and corrosion protection was subsequently evaluated, using pull-off adhesion tests and electrochemical measurements. The results demonstrated that HNT was uniformly dispersed in the epoxy via a sequential process consisting of ultrasonic agitation in a solvent, mechanical stirring, and subsequent ultrasonication in the epoxy mixture. Experimental results indicated that epoxy coatings incorporating HNT exhibited 1.84–2.64 times higher adhesion strength than neat epoxy coatings, with adhesion increasing progressively as HNT content rose from 1 to 3 wt.% and showing negligible variation upon further increase to 5 wt.%. Moreover, the corrosion rate of carbon steel was markedly reduced in the presence of HNT, reaching a minimum value of 0.0328×10^{-3} mm/y at 3 wt.% HNT loading. It was shown that a relatively low HNT loading was sufficient to enhance adhesion strength and corrosion resistance of epoxy coatings, highlighting the potential of this nanomaterial for protective coatings.

Keywords: Corrosion; Epoxy coating; Halloysite; Adhesion; Dispersion.

1. INTRODUCTION

Corrosion is one of the primary causes of damage and reduced service life of metallic structures, and it is particularly severe in tropical coastal environments such as Vietnam [1]. To mitigate its effects, various protective methods have been employed, among which epoxy coatings are the most widely used due to their ease of application and low cost. However, after prolonged use, epoxy coatings tend to develop cracks or microchannels that facilitate the ingress of corrosive agents [2].

Surface functionalization or the incorporation of nanofillers are common strategies to enhance coating performance. Nanoparticles act as fillers that occupy voids within the structure, thereby improving corrosion resistance and reinforcing the physicomechanical properties of epoxy coatings [3]. Halloysite nanotubes (HNT) are naturally occurring nanomaterials with a hollow tubular structure, featuring inner diameters below 100 nm and typical lengths of 0.5-1.2 μm [4]. At low loading levels, HNT uniformly disperses and contributes to the formation of cross-linked networks, hindering polymer chain mobility and establishing strong interfacial interactions with epoxy. Consequently, they enhance physicomechanical properties such as hardness, tensile strength, and thermal stability of the coating matrix [5, 6]. Conversely, at high loadings, HNT tend to aggregate, resulting in poor interfacial interactions, deterioration of mechanical properties, and defects within the nanocomposite structure [7].

Beyond their role as fillers, HNT are also employed as nanocarriers for corrosion inhibitors

owing to their hollow morphology, which allows for the efficient encapsulation of compounds such as benzimidazole (BI) and benzotriazole (BTA). Coatings containing BI and BTA have been reported to achieve impedance values of 2.4×10^7 and 8.5×10^7 $\Omega\cdot cm^2$, respectively, which are substantially higher than those of the neat epoxy coating [8, 9].

However, the direct influence of HNT on the intrinsic performance of epoxy coatings has been scarcely reported. This study focuses on assessing the dispersion behavior and stability of HNT in epoxy matrices, as well as evaluating the effect of HNT loading on the adhesion strength and corrosion resistance of epoxy coatings on carbon steel.

2. EXPERIMENTAL

2.1. Experimental materials

Raw halloysite nanotubes (HNT) were purchased from Guang Zhou Shinshi Metallurgy and Chemical Co., Ltd. (China). Enikon epoxy resin (X75) and polyamine curing agent C225 were supplied by TOP ONE Joint Stock Company (Vietnam). N-Butyl acetate (BA) solvent was purchased from Xilong (China), and ethanol was obtained from Cemaco (Vietnam). Carbon steel CT3 was used as the substrate material for the coatings.

The raw HNT were mixed with distilled water at a 1:10 ratio, stirred for 30 min, and allowed to settle for 10 min to remove black residues at the bottom. The supernatant was then centrifuged for 15 min to collect the sediment-free solid fraction. The obtained solid was dried at 110 °C, cooled, and subsequently ground into a fine powder, yielding the treated HNT. All experiments in this study were conducted using this treated HNT.

2.2. Experimental methods

2.2.1. Procedure for dispersing HNT in epoxy resin mixtures

Halloysite nanotubes (1 wt.%) were dispersed in an epoxy resin mixture using three different procedures, as described below:

Procedure 1: The X75/BA and HNT/BA mixtures were prepared separately at weight ratios of 25/5 and 0.5/7.5, respectively, followed by mechanical stirring for 15 min. The two mixtures were then combined and further mechanically stirred for 45 min. The final mixture is designated as sample M1.

Procedure 2: Epoxy and BA were premixed, followed by the addition of HNT. The resulting mixture was mechanically stirred for 15 min and then ultrasonicated for 30 min.

Procedure 3: HNT was first ultrasonically dispersed in BA for 15 min, then mixed with epoxy/BA. The combined mixture was subsequently stirred mechanically for 15 min and ultrasonicated for 30 min.

2.2.2. Preparation of epoxy coatings on carbon steel substrates

a) Neat epoxy mixture: Epoxy resin and curing agent were separately mixed with BA and stirred mechanically for 15 min to form component D1 (epoxy resin/BA at a weight ratio of 100/50) and component D2 (curing agent/BA at a weight ratio of 25/12.5). These two components were then combined and mechanically stirred for an additional 15 min to obtain the neat epoxy mixture (without HNT).

b) Epoxy/HNT mixture: Epoxy resin was mixed with BA at a weight ratio of 100/15 and mechanically stirred for 15 min to obtain component C1. In parallel, HNT were dispersed in 35 wt.% BA solution and subjected to ultrasonic treatment for 15 min to form component C2. Components C1 and C2 were then combined, stirred for 15 min, and ultrasonicated for 30 min to yield component M3. Separately, curing agent C225 was mixed with BA at a weight ratio of 2/1 and mechanically stirred for 15 min to produce component N3. Finally, M3 and N3 were combined at a weight ratio of 4/1 and mechanically stirred for 15 min to obtain the epoxy mixture containing HNT.

c) Preparation of epoxy coatings on steel substrates: CT3 steel specimens with dimensions of 150 × 75 × 1 mm (for electrochemical measurements) and 150 × 75 × 1.5 mm (for adhesion tests) were polished with sandpapers of grit 180 and 320 to remove surface rust, followed by cleaning with ethanol. The neat epoxy and the HNT-loaded epoxy mixtures (prepared using the above procedures) were applied onto the steel substrates via dip-coating. The coated samples were dried under ambient conditions for 72 h and stored. The designations of the test samples are listed in table 1.

Table 1. *Designations of test samples.*

Sample	Adhesion Test	Electrochemical Test
Neat epoxy	HNT0-PO	HNT0-LSV
Epoxy with 1 wt% HNT	HNT1-PO	HNT1-LSV
Epoxy with 2 wt% HNT	HNT2-PO	HNT2-LSV
Epoxy with 3 wt% HNT	HNT3-PO	HNT3-LSV
Epoxy with 4 wt% HNT	HNT4-PO	HNT4-LSV
Epoxy with 5 wt% HNT	HNT5-PO	HNT5-LSV

2.2.3. Characterizations

a) Dispersion efficiency: The dispersion of HNT in epoxy was evaluated by visually inspecting photographs of the HNT/epoxy mixtures and comparing the HNT sedimentation.

b) Adhesion: Adhesion tests were conducted according to ISO 16276–1:2007. The testing area and dolly surface were lightly sanded, and the dolly was attached to the coating using an epoxy–cyanoacrylate adhesive (1:1). Samples were stored at 23 ± 2 °C and 50 ± 5% relative humidity for 24 h. Coating outside the test area was then removed, and the pull-off force was measured using a PosiTest AT - a device at a loading rate of 0.2 MPa/s until the coating detached.

c) Corrosion rate: Electrochemical measurements were performed using an Autolab PGSTAT30 system with a three-electrode configuration: the coated steel plate as the working electrode, a stainless steel counter electrode, and a saturated Ag/AgCl/KCl reference electrode. Coated samples were immersed in 3.5% NaCl solution for 24 h. When the open-circuit potential (E_{OCP}) stabilized, linear sweep voltammetry (LSV) was performed within a potential range of E_{OCP} ± 0.4 V at a scan rate of 10 mV/s. Corrosion potential and current were determined by Tafel extrapolation from the polarization curves. The corrosion rate (CR) was calculated based on Faraday's law using the following equation (1):

$$CR = \frac{M}{nF\rho} \times i_{corr} \quad (1)$$

Where: M: The molar mass of the substrate metal;
ρ: The density of the substrate metal;
n: The number of electrons exchanged during the corrosion reaction;
F: The Faraday constant;
i_{corr}: The corrosion current density.

3. RESULTS AND DISCUSSION

3.1. Dispersion of HNT in epoxy

Figures 1a-c show the time-dependent photographs of samples M1, M2, and M3, respectively. For sample M1, where only mechanical stirring was applied, HNT showed poor dispersion with visible sedimentation after 15 min and almost complete settling within 1 h (figure 1a). This phenomenon can be attributed to particle aggregation driven by surface energy minimization, while mechanical stirring was insufficient to break down the agglomerates [10].

In contrast, ultrasonication in sample M2 significantly improved dispersion, although sediment

still appeared after 24 h (figure 1b). During ultrasonication, the continuous formation, growth, and collapse of cavitation bubbles within and around the agglomerates provide sufficient energy to fragment them into smaller particles and detach individual nanotubes, enhancing dispersion compared to mechanical stirring [11].

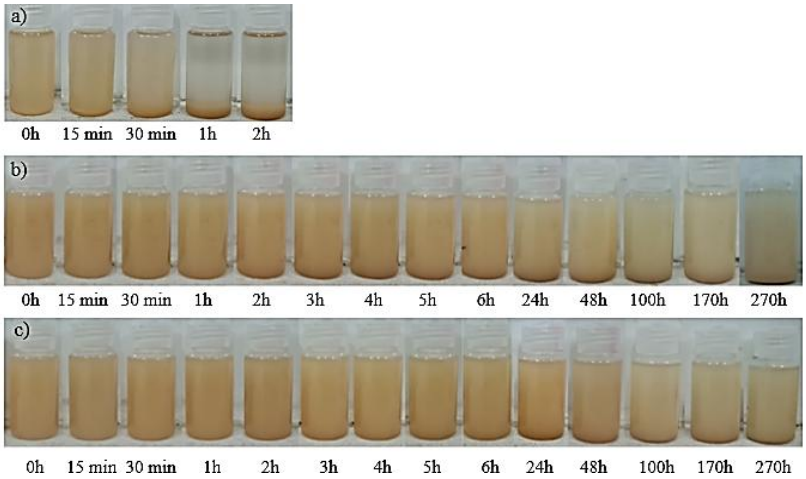

Figure 1. *Time-dependent photograph of samples (a) M1, (b) M2, and (c) M3.*

Sample M3, prepared by ultrasonically pre-mixing HNT in BA prior to incorporation into epoxy, exhibited markedly improved stability, with only slight sedimentation observed after 24 h (figure 1c). This pre-dispersion step enhanced solvent-nanotubes interaction, reduced agglomeration, and yielded smaller aggregates, resulting in improved long-term stability [12].

It can be concluded that pre-dispersing HNT in solvent by ultrasonication, followed by sequential mechanical stirring and ultrasonication with epoxy (procedure 3), provided the most effective dispersion and was therefore selected as the optimal method for preparing HNT-loaded epoxy coatings.

3.2. Effect of HNT loading on the adhesion of epoxy coatings on carbon steel

The adhesion test results of the coatings at three different positions are summarized in table 2.

Table 1. *Adhesion measurement results of coating samples.*

Sample	Adhesion at position 1 (MPa)	Adhesion at position 2 (MPa)	Adhesion at position 3 (MPa)	Average adhesion (MPa)
HNT0-PO	1.38	1.70	1.83	1.64 ± 0.23
HNT1-PO	2.49	3.23	3.41	3.04 ± 0.49
HNT2-PO	2.62	2.84	3.55	3.00 ± 0.49
HNT3-PO	3.70	3.75	4.31	3.92 ± 0.34
HNT4-PO	2.64	3.12	4.71	3.49 ± 1.08
HNT5-PO	2.83	4.97	5.14	4.31 ± 1.29

In addition, the incorporation of HNT led to a marked improvement in adhesion strength, increasing by 1.84 times (HNT2-PO) to 2.64 times (HNT5-PO) compared with the neat sample [13, 14]. The enhancement observed with HNT was greater than that obtained with fly ash (1.1 times), comparable to CNTs (2.65 times), and lower than nano Al_2O_3 and TiO_2 (4.83 and 4.33 times, respectively) [15-17]. At a loading below 3 wt.%, HNT was uniformly dispersed, forming a crosslinked network within the coating, which increased the microscale roughness, thereby enhancing the interfacial adhesion between epoxy and steel substrates. In contrast, at loadings above 3 wt.%, uneven dispersion and weakened interfacial interactions resulted in non-uniform adhesion, as reflected by the larger standard deviations [18, 19].

3.3. Effect of HNT loading on the corrosion protection of epoxy coating on carbon steel

The electrochemical measurement results are presented as polarization curves in figure 2, and the corresponding parameters, including corrosion potential (E_{corr}), corrosion current density (i_{corr}), and corrosion rate (CR), are summarized in table 3. The corrosion potential of neat epoxy-coated carbon steel was -0.56 V, with a corrosion current density of 1.35×10^{-8} A/cm^2. The corrosion potential of HNT-loaded samples remained nearly unchanged relative to the neat epoxy, except at 4 wt.% HNT, while the corrosion current density decreased in all loading samples, confirming enhanced corrosion resistance.

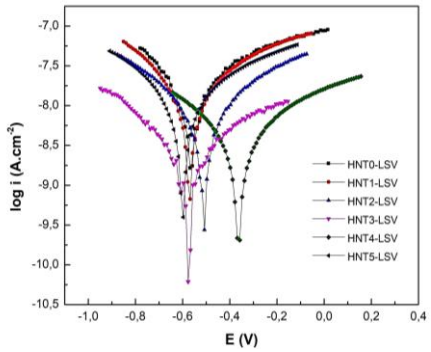

Figure 2. *Polarization curves of the samples.*

The corrosion current density of carbon steel coated with epoxy/HNT in this study was lower than that of epoxy coatings incorporating other nanofillers such as Al_2O_3 and ZnO [20-22]. The addition of HNT created an effective barrier, reducing the porosity of the coating matrix and generating zigzag micropores that impeded the diffusion of corrosive species, which enhanced the corrosion protection performance of the coating [23, 24]. In addition, increasing the HNT content from 1 wt.% to 3 wt.% improved coating adhesion and concurrently reduced the corrosion rate. This enhancement in adhesion reflected stronger interfacial interactions between the coating and the steel substrate, contributing to greater stability and integrity of the coating and limiting underfilm corrosion [25].

Table 2. *Electrochemical parameters and corrosion rates of the samples.*

Sample	E_{corr} (V)	i_{corr} (A/cm^2)	CR (mm/y)
HNT0-LSV	-0.560	1.35×10^{-8}	0.1566×10^{-3}
HNT1-LSV	-0.568	9.86×10^{-9}	0.1144×10^{-3}
HNT2-LSV	-0.509	7.57×10^{-9}	0.0878×10^{-3}
HNT3-LSV	-0.587	2.83×10^{-9}	0.0328×10^{-3}
HNT4-LSV	-0.366	5.43×10^{-9}	0.0630×10^{-3}
HNT5-LSV	-0.595	6.87×10^{-9}	0.0797×10^{-3}

The corrosion rate decreased with increasing HNT loading from 1 to 3 wt.%, but increased again at higher contents. The epoxy coating with 3 wt.% HNT (HNT3-LSV) exhibited the lowest corrosion rate of 0.0328×10^{-3} mm/y, which was 4.77 times lower than that of the neat epoxy coating.

At low filler loadings, strong interfacial interactions between the epoxy and the nanofillers reduced internal stresses and microcrack formation. They also prevented the development of crack channels during curing and led to the formation of additional barrier layers or increased diffusion path length for corrosive agents. At a loading of 3 wt.%, in addition to enhancing adhesion, the nanotubes also filled surface and internal defects in the coating, producing a smoother surface that limited the penetration of corrosive agents. However, at higher loadings, poor dispersion and particle agglomeration introduced structural defects, which could act as pathways for corrosive species to penetrate through the coating and reach the metal substrate [26].

4. CONCLUSIONS

The influence of HNT on the adhesion and corrosion protection performance of epoxy coatings on carbon steel was investigated. Among the three procedures examined, ultrasonic pre-dispersing HNT in the solvent provided the most effective dispersion. The presence of a low HNT loading (1–5 wt.%) increased the adhesion strength of epoxy coatings on CT3 steel by 1.84 to 2.64 times compared to neat epoxy. Furthermore, HNT significantly improved the corrosion resistance of the epoxy coatings, with the 3 wt.% HNT sample exhibiting the lowest corrosion rate of 0.0328×10^{-3} mm/y, which was 4.77 times lower than that of the neat epoxy coating. These results highlight the potential of HNT as a highly effective additive for enhancing the protective performance of epoxy coatings on carbon steel.

Acknowledgments: *The authors gratefully acknowledge the Institute of Tropical Technology for their comprehensive support throughout this study.*

REFERENCES

[1]. B. E. Ibrahimi, J. V. Nardeli, and L. Guo, "*Sustainable corrosion inhibitors I: Fundamentals, methodologies, and industrial applications*," American Chemical Society, pp. 1-19, (2021).

[2]. I. Chopra *et al.*, *"Recent advances in epoxy coatings for corrosion protection of steel: Experimental and modelling approach—A review,"* Materials Today: Proceedings, Vol. 62, (2022).

[3]. G. Cui *et al.*, *"A comprehensive review on smart anti-corrosive coatings,"* Progress in Organic Coatings, Vol. 148, pp. 105821, (2020).

[4]. A. C. Santos *et al.*, *"Halloysite clay nanotubes for life sciences applications: From drug encapsulation to bioscaffold,"* Advances in Colloid and Interface Science, Vol. 257, pp. 58-70, (2018)

[5]. A. I. Idumah *et al.*, *"Recently emerging advancements in halloysite nanotubes polymer nanocomposites,"* Composite Interfaces, Vol. 26, No. 9, pp. 751-824, (2019).

[6]. H. Vahabi et al., *"Flame retardant epoxy/halloysite nanotubes nanocomposite coatings: Exploring low-concentration threshold for flammability compared to expandable graphite as superior fire retardant,"* Progress in Organic Coatings, Vol. 119, pp. 8-14, (2018).

[7]. G. Ravichandran *et al.*, *"Enhancement of mechanical properties of epoxy/halloysite nanotube (HNT) nanocomposites,"* SN Applied Sciences, Vol. 1, No. 4, p. 296, (2019).

[8]. Y. Liu *et al.*, *"A novel dual-responsive halloysite nano-container for anti-corrosion coatings*," Anti-Corrosion Methods and Materials, Vol. 69, (2022).

[9]. K. Zahidah *et al.*, *"Benzimidazole-loaded halloysite nanotube as a smart coating application,"* International Journal of Engineering and Technology Innovation, Vol. 7, pp. 243-254, (2017).

[10]. L. Lisuzzo *et al.*, *"Colloidal stability of halloysite clay nanotubes,"* Ceramics International, Vol. 45, No. 2, pp. 2858-2865, (2019).

[11]. S. Srivastava, A. Pandey, and M. Agarwal, *"Metallurgical evaluation of halloysite-epoxy composite processed by ultrasonication,"* Materials Today: Proceedings, Vol. 49, pp. 239-242, (2022).

[12]. T. Ngo *et al.*, *"Effect of temperature, duration and speed of pre-mixing on the dispersion of clay/epoxy nanocomposites,"* Composites Science and Technology, Vol. 69, pp. 1831-1840, (2009).

[13]. N. T. Anh, *et al.*, *"Influence of hydrotalcite containing corrosion inhibitor modified by silane on corrosion protection performance of epoxy coating,"* VNU Journal of Science: Natural Sciences and Technology, Vol. 33, No. 4, (2017).

[14]. T. Anh Truc *et al.*, *"Improvement of adherence and corrosion protection properties of an epoxy-polyamide coating on steel by incorporation of an indole-3 butyric acid-modified nanomagnetite,"* Journal of Coatings Technology and Research, Vol. 13, pp. 489-499, (2016).

[15]. P. Chen *et al.*, *"Adhesion and erosion properties of epoxy resin composite coatings reinforced with fly ash cenospheres and short glass fibers,"* Progress in Organic Coatings, Vol. 125, pp. 489-499, (2018).

[16]. A. M. El Saeed, M. A. E. Fattah, and M. M. Dardir, *"Synthesis and characterization of titanium oxide nanotubes and its performance in epoxy nanocomposite coating,"* Progress in Organic Coatings, Vol. 78, pp. 83-89, (2015).

[17]. L. L. Zhai, G. Ling, and Y. Wang, *"Effect of nano-Al_2O_3 on adhesion strength of epoxy adhesive and steel,"* International Journal of Adhesion and Adhesives, Vol. 28, pp. 23-28, (2008).

[18]. J. P. B. van Dam *et al.*, *"Effect of surface roughness and chemistry on the adhesion and durability of a steel-epoxy adhesive interface,"* International Journal of Adhesion and Adhesives, Vol. 96, pp. 102450, (2020).
[19]. J. H. Kim *et al.*, *"Improvement adhesion durability of epoxy adhesive for steel/carbon fiber-reinforced polymer adhesive joint using imidazole-treated halloysite nanotube,"* Advanced Composites and Hybrid Materials, Vol. 8, No. 1, pp. 135, (2025).
[20]. S. W. Yap *et al.*, *"Superhydrophobic zinc oxide/epoxy coating prepared by a one-step approach for corrosion protection of carbon steel,"* Journal of Materials Research and Technology, Vol. 25, pp. 5751-5766, (2023).
[21]. R. Hsissou *et al.*, *"New epoxy composite polymers as a potential anticorrosive coatings for carbon steel in 3.5% NaCl solution: Experimental and computational approaches,"* Chemical Data Collections, Vol. 31, p. 100619, (2021).
[22]. X. Lu *et al.*, *"Corrosion protection of hydrophobic bisphenol A-based polybenzoxazine coatings on mild steel,"* RSC Advances, Vol. 6, pp. 5805-5811, (2016).
[23]. D.V. Amaral Ceretti *et al.*, *"The role of dispersion technique and type of clay on the mechanical properties of clay/epoxy composites,"* Macromol. Symp., Vol. 383, No. 1, p. 1800055, (2019).
[24]. P. Vijayan, Y. M. Hany El-Gawady, and M. A. S. A. Al-Maadeed, *"Halloysite nanotube as multifunctional component in epoxy protective coating,"* Industrial & Engineering Chemistry Research, Vol. 55, No. 42, pp. 11186-11192, (2016).
[25]. S. G. Croll, *"Surface roughness profile and its effect on coating adhesion and corrosion protection: A review,"* Progress in Organic Coatings, Vol. 148, pp. 105847, (2020).
[26]. M. Shukla and K. Sharma, *"Effect of carbon nanofillers on the mechanical and interfacial properties of epoxy-based nanocomposites: A review,"* Polymer Science Series A, Vol. 61, pp. 439-460, (2019).

TÓM TẮT

Nghiên cứu ảnh hưởng của ống nano halloysit đến khả năng bám dính và hiệu quả bảo vệ ăn mòn thép cacbon của lớp phủ epoxy

Ống nano halloysit (HNT) là một khoáng vật tự nhiên có trữ lượng lớn, thường được sử dụng để làm chất mang ức chế ăn mòn cho lớp phủ. Tuy nhiên, ảnh hưởng trực tiếp của HNT đến tính chất cơ lý và khả năng chống ăn mòn của lớp phủ lại ít được đề cập đến. Nghiên cứu này đầu tiên xây dựng quy trình phân tán HNT trong chất tạo màng epoxy, sau đó đánh giá ảnh hưởng của hàm lượng HNT đến độ bám dính và khả năng chống ăn mòn của lớp phủ epoxy trên nền thép cacbon bằng phương pháp thử bóc tách và phép đo điện hóa. Kết quả cho thấy HNT phân tán đồng đều trong epoxy bằng một quy trình bao gồm khuấy siêu âm trong dung môi trước sau đó lần lượt khuấy cơ và siêu âm trong epoxy. Kết quả thử nghiệm cho thấy, lớp phủ epoxy chứa HNT có độ bám dính cao hơn 1,84 đến 2,64 lần so với lớp phủ không có HNT, độ bám dính tăng dần khi hàm lượng HNT tăng từ 1-3%KL và thay đổi không rõ rệt khi hàm lượng HNT tăng từ 3-5%KL. Tốc độ ăn mòn thép cacbon giảm xuống rõ rệt khi có mặt HNT, đạt giá trị thấp nhất $0{,}0328\times10^{-3}$ mm/năm ở hàm lượng 3%KL HNT. Có thể thấy chỉ với một hàm lượng nhỏ HNT đã góp phần tăng độ bám dính và tăng cường khả năng chống ăn mòn, cho thấy tiềm năng ứng dụng của vật liệu nano này trong lớp phủ epoxy.

Từ khoá: Ăn mòn; Lớp phủ epoxy; Halloysit; Bám dính; Phân tán.