SYNTHESIS OF LAYERED DOUBLE HYDROXIDES NANOCONTAINERS FOR ENHANCED THE CORROSION PROTECTION OF EPOXY COATING

Đến toà soạn: 02-07-2024

Phan Minh Vuong[1,3]*, Pham Quynh Nhu[1], Tran Thi Kim Thoa[1],
Nguyen Chi Cuong[4], Phan Thanh Thao[1,3], To Thi Xuan Hang[2,3]
[1]Institute of Chemical Technology, Vietnam Academy of Science and Technology
[2]Institute for Tropical Technology, Vietnam Academy of Science and Technology
[3]Graduate University of Science and Technology, Vietnam Academy of Science and Technology
[4]Southern Branch of the Joint Vietnam-Russia,
Tropical Science and Technology Research Center
*E-mail: pmvuong@ict.vast.vn

TÓM TẮT

TỔNG HỢP VẬT LIỆU HYDROXIDE LỚP KÉP NHẰM CẢI THIỆN HIỆU QUẢ BẢO VỆ CHỐNG ĂN MÒN CỦA LỚP PHỦ EPOXY

Vật liệu hydroxide lớp kép (LDH) thường được sử dụng như một bình chứa nano (nanocontainer) có khả năng mang và giải phóng anion ức chế ăn mòn khi tiếp xúc với môi trường xâm thực. Với kích thước hạt đồng nhất, LDH siêu mỏng có thể mang một lượng lớn các chất ức chế hữu cơ và duy trì mức độ bảo vệ cao cho thép carbon. Trong nghiên cứu này, hệ vật liệu LDH nanocontainer cấu trúc siêu mỏng mang ức chế ăn mòn 2-benzothiazolythio-succinic acid (LDH-BTSA-ns) được tổng hợp và trong chế tạo lớp phủ bảo vệ chống ăn mòn trên cơ sở epoxy. Kết quả cho thấy vật liệu nano LDH-BTSA-ns với hình thái và kích thước đồng nhất (~145,6 ± 1,4 nm) có tải lượng ức chế ăn mòn (~37,5 wt%) cao hơn với vật liệu dạng khối (32,4 wt%). Điện cực thép carbon ngâm trong dung dịch NaCl chứa LDH-BTSA-ns 3 g/L có thế ăn mòn -439,5 mV, mật độ dòng ăn mòn 1,86 µA.cm^2. LDH-BTSA-ns thể hiện đặc tính ức chế ăn mòn anode. Hệ vật liệu LDH nanosheet đã nâng cao tính chất cơ lý và hiệu quả bảo vệ của lớp phủ epoxy. Sau 21 ngày ngâm trong dung dịch NaCl 3%, modul tổng trở Z_{100mHz} của Ep/LDH-BTSA-ns duy trì ở 1.10^9 Ω.cm^2 cao hơn 5 lần so với Ep-0 và 20 lần so với Ep/LDH-BTSA.

Từ khoá: *Hydroxide lớp kép, bình chứa nano, ức chế ăn mòn hữu cơ, bảo vệ chống ăn mòn, lớp phủ epoxy*

1. INTRODUCTION

Normally, corrosion inhibitors are directly added to the coating formulation to enhance the corrosion protection provided by traditional coatings. However, this approach can result in undesired reactions between the coating components and inhibitor species, resulting in a loss of inhibitor activity and coating degradation [1,2]. To overcome these problems, many researchers developed a new type of material called nanocontainer, which used a host system for carrying desired inhibitors [2,3]. The inhibitors released to the cracked areas when the coating degrades and corrosion processes commence were designed to be stored in the interlayers region of layered double hydroxide (LDH) material. Compared with other nanocontainers, LDH can improve the coating system's overall barrier properties and adhesion effect even after the inhibitor is completely released [4].

However, despite numerous studies that have been published on using nanocontainers for anti-corrosion applications, there is still rare research on loading organic inhibitors into the interlayer regions of LDH while ensuring uniform distribution of lateral size, which is the critical factor for building multipurpose structures in the field of anti-corrosion. In our previous study, the LDH nanosheet loaded 2-benzothiazolythio-succinic acid (BTSA) with a uniform particle size was synthesized, and the anti-corrosion effect was evaluated [5]. The resulting LDH nanocontainer revealed good efficiency in maintaining the anti-corrosion effect on carbon steel electrodes over time. However, the potential for applying an LDH nanocontainer with uniform lateral size in a polymer matrix has not yet been clarified.

This study focuses on the efficiency of the corrosion protection of ultrathin LDH nanosheet loading with organic inhibitor (LDH-BTSA-ns) through an anion exchange method and LDH-BTSA in bulk form (LDH-BTSA) synthesized using the traditional co-precipitation technique. Both types of nanocontainers were applied as a filler to prepare the epoxy coating on S45C carbon steel. The impedance results show that LDH-BTSA-ns enhanced the barrier and adhesion effect of the epoxy coating, leading to the marked corrosion protection of the organic coating membrane.

2. EXPERIMENT

2.1 Preparation of LDH nanocontainer

LDH-BTSA-ns was synthesized through the anion exchange method, as mentioned in our previous study [5]. To conduct an anion exchange reaction, 500 mL of Na_2BTSA 0.02 M in ethanol was placed in a reaction flask with 60 mL of LDH nanosheet (LDH-ns) suspension (40 g/L) added under N_2 stream and reflux at 65°C. The product was centrifuged, cleaned with ethanol, and vacuum-dried at 55°C.

LDH nanocontainer in the bulk form (LDH-BTSA) was synthesized through the co-precipitation method as follows: 200 mL of an alkaline solution (0.48 mol NaOH and 0.1 mol Na_2BTSA) was added into 200 mL of a salt solution (0.1 mol $MgCl_2$ and 0.05 mol $AlCl_3$). The pH is maintained at 9.5 by NaOH 2.4 M solution. The precipitate is filtered and washed with deionized water before hydrothermal treatment at 125°C for 24 hours. The LDH-BTSA product is washed with DI water and alcohol and vacuum-dried at 55°C before analyzing its physical and chemical properties.

2.2 Preparation of epoxy coating

The epoxy coating was prepared using the following procedure: The nanocontainer was added to the epoxy solution (DER 671-X75) at a ratio of 3 wt% and mixed using a magnetic stirrer and ultrasound for 8 hours. Then, the curing solution (XUS 19036.00) was added to the epoxy/LDH suspension at a mass ratio of 1:16. The homogeneous mixture was dip-coated onto prepared steel (100 x 150 x 2 mm) to create a protective anti-corrosion coating. After 14 days of curing, the carbon steel coated epoxy was collected and noted based on the filler composition, i.e. Ep/LDH-BTSA-ns.

2.3 The characterization method

The morphology of LDH was observed on SEM (Hitachi SU-8010, Japan). BTSA intercalated in LDH were measured by UV-Vis spectroscopy (Jasco V630, Japan). The corrosion inhibition effect of LDH was evaluated through Tafel plot, and corrosion resistance performance of epoxy coating was determined through electrochemical impedance spectroscopy (EIS) using VSP300 potentiostat (Biologic). The visual corrosion effect of the coating membrane on carbon was determined by fog salt spray test CCX3000 (Atlas, USA) according to ASTM B117. The peel-off testing was performed using the cross-cut method (TCVN 2097:2015).

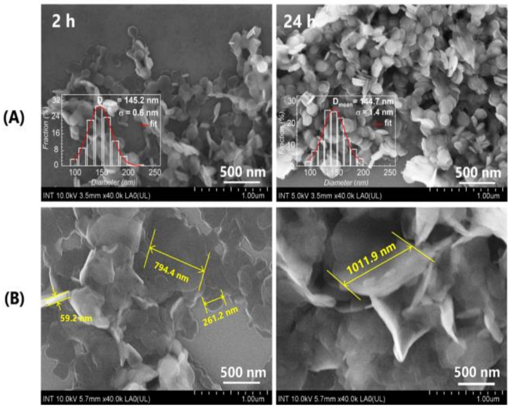
3. RESULTS AND DISCUSSION

3.1 Morphology and compostion of LDH nanocontainer

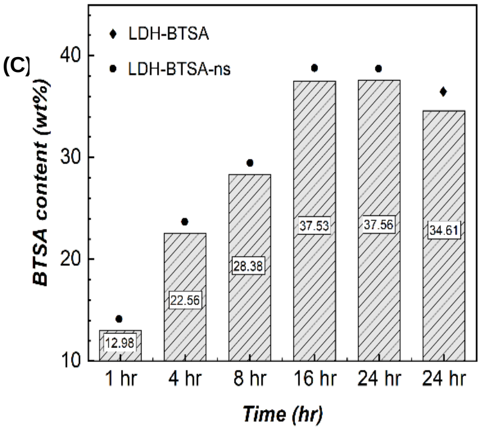
The morphology of LDH-BTSA-ns, as shown in Figure 1A, exhibited the circular nanoplate shape with the particle size centered at 145.2 ± 1.4 nm and did not exhibit any changes in particle size when increasing anion exchange time. This indicated that the anion exchange reaction is a topotactic transformation [6]. The LDH-BTSA from the traditional co-precipitation method was also to compare the morphology and particle size of the nanocontainer. The FE-SEM observation, as depicted in Figure 1B, clearly revealed the disordered morphology of the obtained product, with particle sizes ranging from 100 nm to 1000 nm. The BTSA content in LDH-BTSA-ns by time was determined by UV-vis spectrum at 280 nm and displayed in Figure 1C. The BTSA content was discovered to be 12.98 wt% after one hour of the experiment. After 16 hours, the BTSA content increased significantly to 37.53 wt% and remained stable when increasing reaction time to 24 hours. It should be pointed out that the BTSA content in LDH-BTSA-ns is higher than that synthesized by the traditional co-precipitation process, about 3%.

3.2 The corrosion inhibitor efficiency of LDH nanocontainer

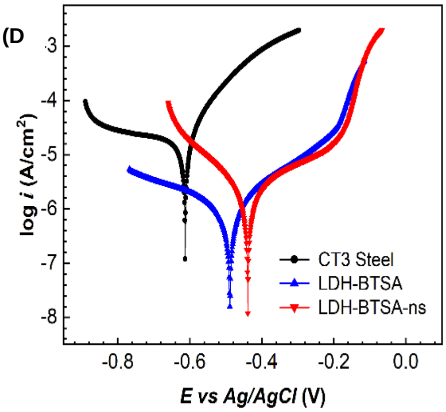
The inhibitor efficiency of the nanocontainers for carbon steel electrodes has been determined using the polarization test. Figure 1D displays the polarisation curves obtained after 2 hours of exposure to the NaCl 0.1 M solution. The blank solution revealed the corrosion potential (E_{corr}) and corrosion current (i_{corr}) at about -613.6 mV and 19.2 µA.cm^2. In comparison to the blank solution, the presence of the lamellar structure of LDH clearly demonstrates a shift in the corrosion potential towards a higher positive value and a lower current density. This confirmed that LDH nanocontainers work as an anodic inhibitor. Compared to LDH-BTSA (-489.8 mV), the solution of LDH-BTSA-ns exhibits a higher E_{corr} at about -439.5 mV and lower current density at about 1.86 µA.cm^2. The corrosion potential was also shifted to greater positive values due to the uniform deposition of positively charged LDH lamellar structure to the anodic area of electrode. This modification may increase the effectiveness of corrosion inhibitors [5,7]. The polarization results indicate that LDH-BTSA and LDH-BTSA-ns have a high level of inhibitor effect of 86% and 91%, respectively.



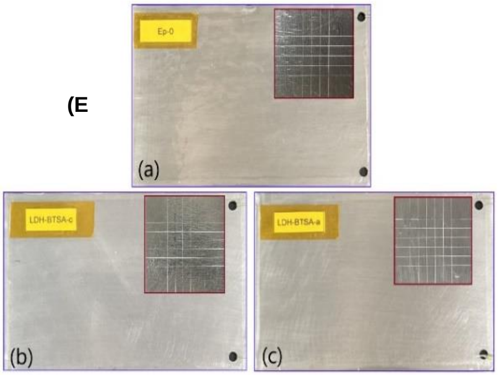
SEM image of (A) LDH-BTSA-ns of 2 and 24 hours anion exchange and (B) LDH-BTSA preparation from traditonal co-precipitation method



The percentage of BTSA intercalated in LDH nanocontainer at different reaction time



Polarization curve of S45C electrodes after 2 hours of immersion in 0.1 M NaCl solution with and without inhibitor and containing 3 g/L of LDH-BTSA-ns and LDH-BTSA



Visual images of the coating films: (a) Ep-0, (b) Ep/LDH-BTSA, and (c) Ep/LDH-BTSA-ns. The images of peef off testing through the cross-cut method (TCVN 2097:2015) was inset.

Figure 1. Morphology and compostion of LDH nanocontainer, the corrosion inhibitor efficiency of LDH nanocontainer and physical properties of epoxy coating

3.3 Physical properties of epoxy coating

The epoxy coatings were dip-coated onto carbon steel plates with 150x100x2 mm dimensions. The film thickness after 14 days of curing was 25 ± 2 µm. Visual analysis showed that the coatings had a similar appearance on carbon steel surfaces (Figure 1E). All of coatings had good adhesion, with smooth edges of the cuts and no peeling observed, classified as grade 0 according to this standard. Ep/LDH-BTSA-ns coating has higher adhesion (2.56 Mpa) than Ep/LDH-BTSA (2.22 Mpa), which can be explained by evenly dispersed nanosheets in the epoxy matrix.The inclusion of LDH filler resulted in an increase in the hardness of the coating (Table 1). This indicates that at a 3% ratio, LDH not only does not hinder the cross-linking process but also acts as a reinforcement for the polymer coating.

Table 1. The physical properties of epoxy coating containg LDH-BTSA and LDH-BTSA-ns nanocontainer

Sample	Adhesion (MPa)	Thickness (μm)	Relative hardness
Ep-0	1.86	25 ± 2	0.68 ± 0,02
Ep/LDH-BTSA	2.22	25 ± 2	0.73 ± 0,05
Ep/LDH-BTSA-ns	2.56	25 ± 2	0.78 ± 0,02

Table 2. The adhension strength, pit dimesion and classified of the epoxy coating after 360 hours of fog salt testing

Sample	Adhesion (MPa)	Pit dimension (μm)	Classified of corrosion protection
Ep-0	0.87	902.61 ± 8.7	6
Ep/LDH-BTSA	1.26	586.3 ± 6.9	8
Ep/LDH-BTSA-ns	1.77	262.7± 4.2	9

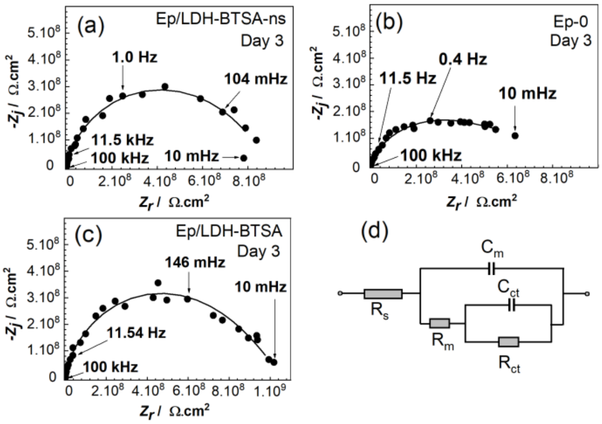


Figure 2. The Nyquist plots of (a) Ep-0, (b) Ep/LDH-BTSA, (c) Ep/LDH-BTSA-ns and(d) circuit diagram of coating samples after 3 days of immersion in a 3% NaCl solution

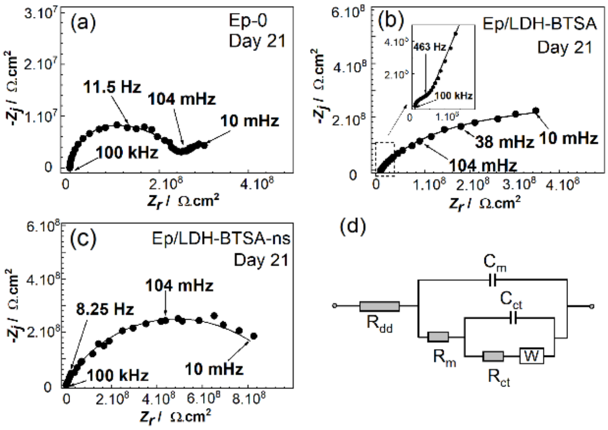


Figure 3. The Nyquist plots of (a) Ep-0, (b) Ep/LDH-BTSA, (c) Ep/LDH-BTSA-ns and(d) circuit diagram of coating samples after 21 days of immersion in a 3% NaCl solution

3.4 The perfomance of epoxy coating containing ultrathin LDH nanocontainer

The effectiveness of epoxy coatings in inhibiting corrosion was examined using electrochemical impedance spectroscopy (EIS) in a 3% NaCl solution at the open circuit voltage. Each measurement was performed in the frequency range from 100 kHz to 10 mHz with 7 points per decade. The Nyquist plot of coating films (exposed surface area 28.26 cm^2) after 3 and 21 days of immersion are displayed in Figures 2, 3.

After 3 days of immersion, the Nyquist impedance of the epoxy coatings exhibited a single time constant at high frequencies (Figure 2). This suggests that the electrolyte permeated the epoxy-covering structure via defects or pores that formed during the curing stage [7]. The current circuit diagram at this stage involves the coating resistance R_m in parallel with the coating capacitance C_m. In addition, the double layer's resistance (R_{ct}) and capacitance (C_{ct}) were present in parallel with the coating resistance (R_m), representing the characteristics of the processes at the metal surface and coating interface [8]. The electrochemical components of the coating are illustrated in Figure 3a, which consists of the coating resistance (R_m) connected in series with the charge transfer resistance (R_{ct}) and in parallel with the capacitor (C_{ct}). The entire system is also connected in parallel with the coating capacitance (C_m). The Nyquist plots of the Ep/LDH-BTSA and Ep/LDH-BTSA-ns samples exhibited a one-time constant with significant closure degrees, indicating the dispersing and shielding capability of the lamellar LDH structure in the epoxy matrix.

After 21 days of immersion, the Nyquist impedance spectra of the Ep-0 and Ep/LDH-BTSA showed the presence of the two-time constants at low frequencies (Figure 3-a,b), indicating that corrosion had occurred on the metal surface [9]. A Warburg impedance (W) is observed in conjunction with the charge transfer resistance (R_{ct}), indicating the diffusion resistance at the metal surface induced by corrosion products [7]. In contrast, EP/LDH-BTSA-ns still revealed one time constant. It indicated the nanosheet system's significant shielding capability on the epoxy coating's corrosion protection effect. The circuit diagram of the system is presented in Figure 3d. It should be noted that the impedance value at a frequency of 100 mHz is a crucial parameter that depicts the electrochemical process occurring at the metal and coated membrane surface [9]. After 21 days of immersion, the Z_{100mHz} value of Ep/LDH-BTSA displayed at about 20.10^7 $\Omega.cm^2$ and significantly higher than Ep-0 (5.10^7 $\Omega.cm^2$). These results suggest the formation of a corrosion-protective layer on the electrode surface. BTSA released from the nanocontainers and absorbed the metal surface, forming a barrier layer that hindered the penetration of NaCl and reduced the rate of metal dissolution reactions at the electrode surface. The Z_{100mHz} value of the Ep/LDH-BTSA-ns sample reached 1.10^9 $\Omega.cm^2$, five times higher than that of Ep/LDH-BTSA and twenty times higher than Ep-0. From these findings, it can be conclude that the LDH-BTSA-ns, which have a uniform ultrathin structure, were tightly arranged in the coating. This arrangement contributed to restoring and protecting the damaged and porous areas in the coating and hindered the movement of the electrolyte solution toward the metal surface [10]. As a result, the coating exhibited a high level of protection.

To further evaluate the protective effectiveness of the paint coatings, the adhesion strength and the width of corrosion pits of the paint coatings after 360 hours of fog salt testing (ASTM B117) were determined. The results of the evaluation of corrosion resistance of the test samples according to ASTM D1654-08 are presented in Table 2. Ep/LDH-BTSA-ns sample exhibited the lowest corrosion pit dimension at about 262.7 ± 4.2 µm, demonstrating the best metal corrosion protection capability among the test samples (level 9). The Ep/LDH-BTSA and Ep-0 have a corrosion pit dimension of 586.3 ± 6.9 µm and 902.61 ± 8.7, achieving a corrosion protection level of 8 and 6, respectively. The differences in corrosion resistance among the test samples were attributed to the uniform distribution of the additive in the polymer matrix. When using LDH-BTSA nanoparticles with uniform shape and size, the corrosion inhibitor could distribute evenly on the coating surface and block defects and voids formed during the sample preparation process. Additionally, when the reinforcing material was uniformly arranged, the released BTSA molecules could uniformly adsorb onto the electrode surface, thereby increasing the adhesion strength of the coating, as demonstrated by peel-off tests. This limited the degradation of the coating caused by penetration.

4. CONCLUSION

The results showed that LDH-BTSA-ns had a high BTSA intercalated (~37.5 wt%) and exhibited anode corrosion inhibition properties. Carbon steel electrodes immersed in NaCl solution containing 3 g/L LDH-BTSA-ns had a corrosion potential of 439.5 mV, corrosion current density of 1.86 µA.cm^2. The incorporation of LDH nanocontainer into the epoxy matrix increased the mechanical properties of coating films. EIS results confirmed that the uniforms of LDH nanosheet have better shielding capabilities when dispersed in the epoxy matrix than the bulk materials. After 3 weeks of immersion in NaCl 3% solution, the Z_{100mHz} of the Ep/LDH-BTSA-ns remained at 1.10^9 Ω.cm^2, 5 times higher than that of Ep/LDH-BTSA (2.10^8 Ω.cm^2) and 20 times higher than Ep-0 (5.10^7 Ω.cm^2). After 360 hours of fog salt testing, Ep/LDH-BTSA-ns revealed the good corrosion protection capability (level 9) according to ASTM D1654-08.

Acknowledgments: The authors are grateful to the Institute of Chemical Technology – VAST for supporting the facilities.

REFERENCES

[1] Poznyak, S., (2009). Novel inorganic host layered double hydroxides intercalated with guest organic inhibitors for anti-corrosion applications. *ACS. Appl. Mater. Interfaces*, **1(10)**, 2353-2362.

[2] Dariva, C. (2014), Corrosion inhibitors–principles, mechanisms and applications. *Developments in corrosion protection*, **16**, 365-378.

[3] Chen Z ., (2023), Micro/nanocontainer-based intelligent coatings: Synthesis, performance and applications–A review. *Chem. Eng. J*, **451**, 138582,

[4] Hang To Thi Xuan, (2015), Effects of hydrotalcite intercalated with corrosion inhibitor on cathodic disbonding of epoxy coatings. *J. Coat. Technol. Res*, **12,** 375-383,

[5] Phan Minh Vuong, (2024), Controllable synthesis of layered double hydroxide nanosheets to build organic inhibitor-loaded nanocontainers for enhanced corrosion protection of carbon steel**,** *Nanoscale Adv.*, **6(2)**, 606-619.

[6] Naik B., (2019), Solvent-mediated and mechanochemical methods for anion exchange of carbonate from layered double hydroxides using ammonium salts. *ACS. Omega*, **4(22)**, 20072-20079.

[7] Abrantes Leal, D., (2020). Zinc-layered hydroxide salt intercalated with molybdate anions as a new smart nanocontainer for active corrosion protection of carbon steel, *ACS. Appl. Mater. Interfaces*, **12(17)**, 19823-19833.

[8] Tabish, M., (2021), Reviewing the current status of layered double hydroxide-based smart nanocontainers for corrosion inhibiting applications. *J. Mater. Res. Technol*,**10**, 390-421.

[9] Li J., (2023). Anti-corrosion mechanism of MgAl-LDHs inhibitors with varying anionic charge on reinforcing steel in simulated concrete pore solutions. *Constr. Build. Mater***,** **363**, 129882.

[10] Liu A., (2018). Delamination and self-assembly of layered double hydroxides for enhanced loading capacity and corrosion protection performance. *Appl. Surf. Sci*, **462**, 175-186.