

# Influence of Hydrotalcite Containing Corrosion Inhibitor Modified by Silane on Corrosion Protection Performance of Epoxy Coating

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**Abstract:** Zinc aluminum hydrotalcite containing 2-benzothiazolythio-succinic acid (HT-BTSA) and modified by 2-aminoethyl-3-aminopropyltrimethoxysilane (APS) at different concentrations (3%, 5% and 10%). APS modified HT-BTSA (HT-BTSA-S) was incorporated in epoxy coatings at 3% concentration. The corrosion protective performance of the epoxy coatings containing HT-BTSA-S were evaluated by electrochemical impedance spectroscopy, adhesion measurement. The results showed that the presence of HT-BTSA-S improved protection performance of epoxy coating and the best protection was obtained with HT-BTSA modified with 5 % APS.

**Keywords:** Epoxy coating, hydrotalcite, silane modification, corrosion inhibitor, corrosion protection.

## 1. Introduction

Organic coatings are widely used for corrosion protection of metal surfaces because they are not expensive and can be easily applied. Chromates are the best corrosion inhibitors for organic coatings, but they are toxic and carcinogenic, so that it is necessary to replace chromates by nontoxic inhibitors. Recently, the use of additives based on hydrotalcites has the attractive attention. Organic coatings containing hydrotalcite intercalated with corrosion inhibitors were studied [1-5]. The effect of hydrotalcites on

protective properties of polymer nanocomposites depends on their dispersion degree in the polymer matrix [6-8]. In order to improve the dispersion of hydrotalcite in polymer matrix, the hydrotalcite surface can be modified by surfactants or silane compounds [9, 10].

In our previous studies, hydrotalcites intercalated with 2-benzothiazolythio-succinic acid (HT-BTSA) was prepared and applied in epoxy coatings. The presence of HT-BTSA improved significantly the corrosion protection of epoxy coating [11, 12]

In this work, hydrotalcites intercalated with 2-benzothiazolythio-succinic acid (HT-BTSA) modified by silane at different concentrations were prepared. Corrosion protection of epoxy

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coatings containing silane modified HT-BTSA was evaluated by electrochemical impedance spectroscopy and adhesion measurements.

## 2. Experimental

### 2.1. Materials

Sodium hydroxide, zinc nitrate hexahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , aluminum nitrate nonahydrate  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 2-aminoethyl-3-aminopropyltrimethoxysilane (APS) were purchased from Merck. Corrosion inhibitor, 2-benzothiazolylthio-succinic acid (BTSA) was obtained from Ciba Company. The epoxy resin was epoxy Bisphenol A, Epotec YD 011-X75, epoxy equivalent weight is about 469-490 g/eq. The hardener PA66 was modified polyamine. Both compounds were purchased from Thai organic chemicals. Co. (Thailand).

### 2.2. Preparation of hydrotalcite intercalated with BTSA

The zinc aluminum hydrotalcite intercalated with BTSA (HT-BTSA) were prepared using the co-precipitation method. A solution of 0.125 mol of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.0625 mol of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 125 ml of degassed distilled water were added to a drop wise solution of 0.313 mol of BTSA with the molar equivalent of NaOH in 145 ml of degassed distilled water with vigorous mixing under an inert nitrogen atmosphere. The pH of the solution was maintained at 8-9 by adding 1M NaOH solution. The resultant slurry was aged at 65°C for 24 h, cooled to room temperature, and repeatedly washed with large amounts of degassed distilled water before drying at a temperature of 50°C for 24 h in a vacuum oven.

### 2.3. Modification of HT-BTSA by 2-aminoethyl-3-aminopropyltrimethoxysilane

Solution 2-aminoethyl-3-aminopropyltrimethoxysilane in ethanol was added drop wise to solution of HT-BTSA in ethanol. The temperature was maintained at

60°C for 6 h. The white precipitate was washed several times with ethanol. HT-BTSA modified by silane was dried at 50°C in a vacuum oven for 24 h. The HT-BTSA modified by at silane concentration of 3%, 5% and 10% and the modified HT-BTSA were named HT-BTSA-S3, HT-BTSA-S5 and HT-BTSA-S10 respectively.

### 2.4. Preparation of epoxy coatings

Carbon steel sheets (150mm×100mm×2mm) were used as substrates. The sheets were polished with abrasive papers from 80 to 600 grades and cleaned with ethanol. The hydrotalcites were incorporated in epoxy coating at 3 %. The hydrotalcites were incorporated in epoxy resin at 3 wt%, the hardener was added to the epoxy solution containing hydrotalcite before the application on carbon steel.

The liquid paint was applied by spin coating at 600 rpm for 1 min and dried at ambient temperature for 7 days. The dry film thickness was  $30 \pm 3 \mu\text{m}$  (measured by Minitest 600 Erichen digital meter).

### 2.5. Analytical characterizations

The FTIR spectra were obtained using the KBr method on a Nexus 670 Nicolet spectrometer operated at  $1 \text{ cm}^{-1}$  resolution in the 400–4000  $\text{cm}^{-1}$  region.

Powder X-ray diffraction patterns of synthesized HTs were taken using Siemens diffractometer D5000 with  $\text{CuK}_\alpha$  radiation (1.5406 Å) at room temperature under air conditions.

### 2.6. Electrochemical characterization

The electrochemical impedance measurements were performed using AUTOLAB P30 over a frequency range of 100 kHz to 10 mHz with six points per decade using 30 mV peak-to-peak sinusoidal voltage. For the electrochemical impedance measurements, a three-electrode cell was used with a large

platinum auxiliary electrode, a saturated calomel reference electrode (SCE) and a working electrode with an exposed area of  $12.56 \text{ cm}^2$ . The corrosive medium was the 3% NaCl solution.

### 2.7. Adhesion measurement

The adhesion strength of the coatings was determined according to ASTM D4541 by a PosiTest digital Pull-Off adhesion tester (DeFelsko) with 20 mm dollies. The experiments involved pulling dollies affixed by a 2-part Araldit<sup>TM</sup> Epoxy adhesive away from the coated substrate. The maximum force by which the dolly lifts the coating from the steel plate was recorded as a measure of the bond strength between the coating and the substrate.

## 3. Results and discussion

### 3.1. Characterization of HT-BTSA modified by APS

HT-BTSA modified by APS was characterized by FT-IR spectroscopy and XRD. Figure 1 shows the FT-IR spectra APS, HT-BTSA, HT-BTSA-S3, HT-BTSA-S5 and HT-BTSA-S10.

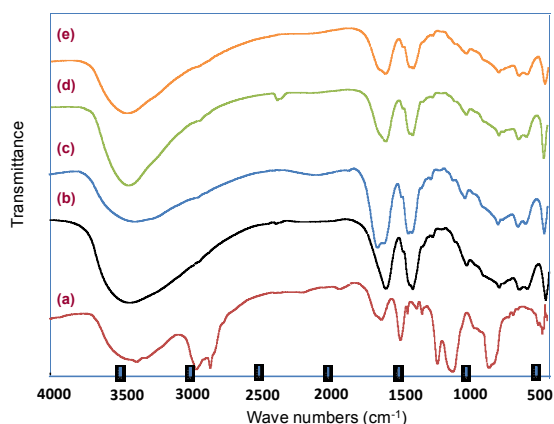


Fig. 1. FT-IR spectra of APS (a), HT-BTSA (b), HT-BTSA-S3 (c), HT-BTSA-S5 (d) and HT-BTSA-S10 (e).

The spectrum of APS shows a band at  $3370 \text{ cm}^{-1}$  characteristic of  $-\text{OH}$  and  $-\text{NH}_2$  groups. The bands at  $2940 \text{ cm}^{-1}$  and  $2840 \text{ cm}^{-1}$  are attributed to the vibration of  $-\text{CH}_3$  and  $-\text{CH}_2$  groups. The band at  $1083 \text{ cm}^{-1}$  is relative to Si-O vibration and characteristic band at  $818 \text{ cm}^{-1}$  originates from the symmetric stretch of Si-O- $\text{CH}_3$  [13].

The spectrum of HT-BTSA displays the characteristic peaks of hydroxalcite at  $423 \text{ cm}^{-1}$ ,  $630 \text{ cm}^{-1}$ . It is observed also the characteristic peak of  $\text{COO}^-$  at  $1580 \text{ cm}^{-1}$  and  $1423 \text{ cm}^{-1}$ .

The spectra of HT-BTSA-S present peaks characteristic of HT-BTSA at  $1383 \text{ cm}^{-1}$  và  $1580 \text{ cm}^{-1}$  which are attributed to  $-\text{NO}_3^-$  và  $\text{COO}^-$  groups. Beside that spectra of HT-BTSA-S show peaks characteristic of Si-O-Al, Si-O-Zn at  $994 \text{ cm}^{-1}$ . These results indicate that APS has been successfully grafted onto the HT-BTSA surface.

Figure 2 shows the XRD patterns of HT-BTSA, HT-BTSA-S3, HT-BTSA-S5 and HT-BTSA-S10. The XRD patterns of the HT-BTSA exhibit the (003) reflection corresponding to the basal spacing of hydroxide layer of 1.73 nm, which is higher than the value of zinc aluminum nitrate hydroxalcite of 0.79 nm [12]. The higher d-spacing values of the HT-BTSA by comparison with this value of nitrate hydroxalcite show that molybdate were intercalated in the interlayer domain and replaced  $\text{NO}_3^-$  anion. The XRD pattern of HT-BTSA-S3 has the peaks corresponding to the d-spacing of 0.82 nm and 1.66 nm, similarly to the one of HT-BTSA. This results indicate that in the case of HT-BTSA-S3, the APS was grafted on the external surface of hydroxalcite. For HT-BTSA-S5 and HT-BTSA-S10 the interlayer distance were slightly increased. The increase of interlayer distance of HT-BTSA-S5 and HT-BTSA-S10 shows that the APS was not only grafted on the external surface but also intercalated between hydroxide layers of hydroxalcites.

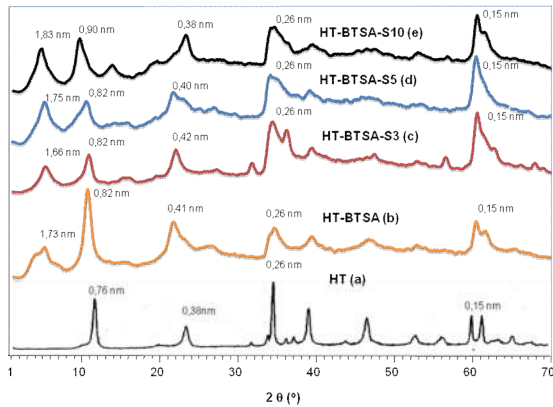


Fig. 2. XRD patterns of HT (a), HT-BTSA (b), HT-BTSA-S3 (c), HT-BTSA-S5 (d) và HT-BTSA-S10 (e).

### 3.2. Electrochemical impedance measurements

EIS measurements were carried out to evaluate the corrosion resistance of the carbon steel covered by the pure epoxy coating and epoxy coating containing HT-BTSA, epoxy coating containing HT-BTSA-S3, epoxy

coating containing HT-BTSA-S5 and epoxy coating containing HT-BTSA-S10 at three concentrations 3 % during immersion time in 3 wt.% NaCl solution. The impedance diagrams obtained after 28 days exposure to 3 % NaCl solution are presented in Fig 3.

After 28 days immersion in 3 % NaCl solution, the EIS diagram of pure epoxy coating presented two circles well defined. This indicates that electrolyte penetrated in the coating and the corrosion process occurred at metal surface. For epoxy coatings containing HT-BTSA, HT-BTSA-S the second cycles at low frequencies were not determined. These results shows that for this coatings electrolyte were not reached the metal surface and the corrosion process did not begin. The impedance modulus of epoxy coating containing HT-BTSA and HT-BTSA-S were higher than this value of pure epoxy coating. Among coatings containing hydrotalcite, coating containing HT-BTSA-S5 had highest impedance modulus.

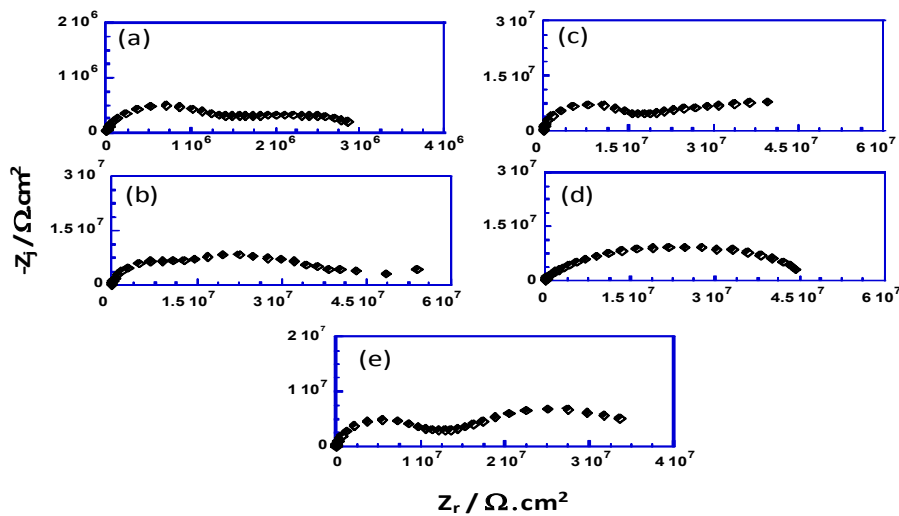


Fig. 3. Electrochemical impedance diagrams obtained after 28 days exposure to 3 % NaCl solution for the carbon steel covered by pure epoxy coating (a), epoxy coating containing 3% hydrotalcite: HT-BTSA (b), HT-BTSA-S3 (c), HT-BTSA-S5 (d) and HT-BTSA-S10 (e).

According to literature, the impedance modulus at low frequency, between 1 and 0.01 Hz, is an appropriate parameter for characterization of corrosion protection of

coatings [14, 15]. The impedance modulus at low frequency of 10 mHz,  $Z_{10\text{mHz}}$  were extracted from impedance diagrams, were used to follow the degradation of coatings with

exposure time in the aggressive solution. The variation of  $Z_{10\text{mHz}}$  values with immersion time in NaCl 3% solution are presented in Fig. 4.

At the beginning, the  $Z_{10\text{mHz}}$  values of all coatings were very high and these values of coatings containing hydrotalcite were higher than the one of pure epoxy coating. During the first 7 days of immersion the  $Z_{10\text{mHz}}$  values of pure epoxy coatings decreased rapidly, while these values of coatings containing hydrotalcite decreased progressively. The decrease of  $Z_{10\text{mHz}}$  values was due to penetration of water and electrolyte in the coatings. After 28 days of exposure, the  $Z_{10\text{mHz}}$  values of coating containing HT-BTSA and coating containing HT-BTSA modified by APS were higher than the one of pure epoxy coating. The  $Z_{10\text{mHz}}$  values containing HT-BTSA modified by APS were higher than the one of epoxy coating containing HT-BTSA. Among coatings containing APS modified HT-BTSA, the epoxy coating containing HT-BTSA-S5 had highest  $Z_{10\text{mHz}}$  values. The results indicate that the presence of HT-BTSA improved the corrosion protection performance of epoxy coating and modified by silane improved the effect of HT-BTSA. The best protection was obtained with the HT-BTSA-S3.

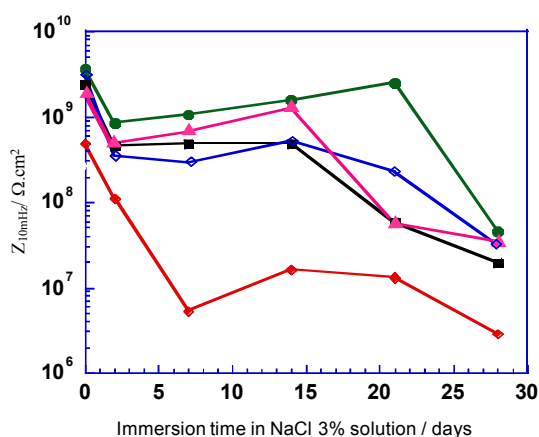


Fig. 4. Variation of  $Z_{10\text{mHz}}$  values with immersion time in NaCl 3% solution of pure epoxy coating (♦), epoxy coating containing 3% hydrotalcite: HT-BTSA (■), HT-BTSA-S3 (◇), HT-BTSA-S5 (●) and HT-BTSA-S10 (▲).

Beside impedance measurement the adhesion of coatings was evaluated (Table 1). It is observed that the adhesion of epoxy coatings containing HT-BTSA is closed to the one of pure epoxy coating. Among coatings containing APS modified HT-BTSA, the coating with HT-BTSA-S3 and HT-BTSA-S5 has higher adhesion strength by comparison with coating containing HT-BTSA. The increase of coating adhesion with the presence of HT-BTSA modified by APS can be explained by the interaction of APS with the steel surface. These adhesion results are in agreement with the impedance measurement.

Table 1. Adhesion strength of coatings

Sample	Adhesion strength (N/mm <sup>2</sup> )
Pure epoxy coatings	0.7
Epoxy coating containing 3% HT-BTSA	0.7
Epoxy coating containing 3% HT-BTSA-S3	0.9
Epoxy coating containing 3% HT-BTSA-S5	0.8
Epoxy coating containing 3% HT-BTSA-S10	0.7

#### 4. Conclusions

Zinc aluminum hydrotalcite containing 2-benzothiazolythio-succinic acid (HT-BTSA) and modified by 2-aminoethyl-3-aminopropyltrimethoxysilane (APS) were successfully prepared. The presence of HT-BTSA and silane modified HT-BTSA improved corrosion resistance epoxy coating. Surface modification by APS enhanced protection efficiency of HT-BTSA on epoxy coatings and the best protection performance was obtained with HT-BTSA modified by 3% APS.

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## Ảnh hưởng của Hydrotanxit mang ức chế ăn mòn biến tính bằng Silan đến hiệu suất bảo vệ ăn mòn của màng Epoxy

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**Tóm tắt:** Hydrotalcit Zn-Al mang axit 2-benzothiazolythio-succinic (HT-BTSA) và được biến tính bằng 2-aminoethyl-3-aminopropyltrimethoxysilane (APS) tại các nồng độ khác nhau (3%, 5% and 10%). HT-BTSA biến tính APS (HT-BTSA-S) được đưa vào màng epoxy với nồng độ 3%. Hiệu suất bảo vệ ăn mòn của màng epoxy chứa HT-BTSA-S được đánh giá bằng phổ tổng trở điện hóa và đo độ bám dính. Kết quả chỉ ra rằng sự có mặt của HT-BTSA-S đã cải thiện khả năng bảo vệ cho màng epoxy và khả năng bảo vệ tốt nhất thu được với màng epoxy chứa HT-BTSA biến tính APS 5%.

*Từ khóa:* Màng epoxy, hydrotanxit, biến tính silan, ức chế ăn mòn, bảo vệ ăn mòn.