

## **INFLUENCE OF GRAPHENE OXIDE ON THE CORROSION INHIBITION EFFECT OF HYDROTALCITE LOADED WITH 2-BENZOTHAZOLYTHIO-SUCCINIC ACID**

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### **ABSTRACT**

Hydrotalcite intercalated with 2-benzothiazolythio-succinic acid and graphene oxide (HT-BTSA/GO) was synthesized by co-precipitation method. Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) were used to characterize obtained HT-BTSA/GO. The release of BTSA from HT-BTSA/GO in NaCl solution at different concentrations was investigated by UV-Vis spectroscopy. HT-BTSA/GO was incorporated in solvent free epoxy coatings at concentration of 1 wt% and the corrosion protection of these coatings on carbon steel were examined by salt spray test and adhesion measurement. It was shown that GO and BTSA were intercalated in hydrotalcite structure and BTSA content was about 19.7 wt%. The release of BTSA from HT-BTSA/GO depended on chloride ion concentrations. After 72 h immersion in 0.1 M and 0.5 M NaCl solutions, the BTSA release were about 19.3 % and 61.0 % respectively. The presence of HT-BTSA/GO improved the corrosion resistance and adhesion of solvent free epoxy coatings. The corrosion protection performance of coatings containing HT-BTSA/GO was higher in comparison to the coating containing HT-BTSA.

**Keywords:** hydrotalcite, 2-benzothiazolythio-succinic acid, graphene oxide, solvent free epoxy coating, corrosion protection.

## 1. INTRODUCTION

Chromate inhibitive species provide the best corrosion protection for metals but they are toxic and so many researches focus on environmentally friendly corrosion inhibition pigments to replace these compounds.

Hydrotalcites with anion exchange ability were studied as the inhibitor carriers for protective coatings [1-5]. They are able to both release corrosion inhibitors and absorb chloride anions from an aggressive environment. Hydrotalcites carrying various inhibitors have been synthesized and applied in different coating systems for corrosion protection of metallic substrates.

The enhancement of mechanical, thermal and barrier behaviors of organic coatings by graphene oxide was studied [6-8]. Recently, hydrotalcite/graphene composites have been much interested by researchers due to their lamellar structure and complementary properties [9-11].

We have studied hydrotalcite containing 2-benzothiazolythio-succinic acid (HTC-BSA) as an additive for organic coatings [12, 13]. HTC-BSA improved the protective properties of organic coating. HTC-BSA/GO was also prepared and its inhibition effect on steel substrate was studied using electrochemical technique. It was found that intercalated GO enhanced inhibition effect of HTC-BSA [14].

The objective of this work is to use synthesized HTC-BSA/GO as container of corrosion inhibitors and study its influence on corrosion resistance and adherence property of the solvent free epoxy coatings. The BSA release from HTC-BSA/GO in sodium chloride solutions was also studied. The corrosion resistance of coatings loading HTC-BSA/GO on carbon steel was studied by salt fog test. The coating adherence was investigated by pull-off test.

## 2. MATERIALS AND METHODS

### 2.1. Materials

2-benzothiazolythio-succinic acid (BSA) was supplied by Ciba Company. Graphite was purchased from Sigma-Aldrich. Zinc nitrate, aluminum nitrate, H<sub>2</sub>SO<sub>4</sub> (95-98 %), KMnO<sub>4</sub> and NaOH were obtained from Merck. A solvent free epoxy Epon 828 (Momentive) and Ancamine 2753 hardener were obtained from Air product. Graphene oxide was prepared in our laboratory using Hummer's procedure [14].

### 2.2. Preparation of HTC-BSA and HTC-BSA/GO

In co-precipitation procedure of HTC-BSA [13], the reaction was carried out in nitrogen atmosphere to eliminate the intercalation of CO<sub>2</sub> in hydrotalcite structure. The mixture 0.125 mol of zinc nitrate and 0.0625 mol of aluminum nitrate in 125 mL degassed distilled water was slowly added to 250 mL of 0.250 mol of BSA in ethanol. The pH of reaction mixture was adjusted and maintained at 8-10. The reaction mixture was kept at 65 °C for 24 h. After that, the precipitate was filtered and washed with degassed distilled water, then dried in a vacuum oven at 50 °C for 24 h.

HTC-BSA/GO was prepared via the similar method as for HTC-BSA except the BSA solution adding GO (GO/HTC weight ratio = 1/20).

### **2.3. Determination of BSA content in HTC-BSA/GO**

The UV–Vis spectroscopy was used to measure the content of BSA in HTC-BSA/GO. The UV–Vis absorbance of BSA at  $\lambda_{\text{max}} = 283$  nm was used for the analysis. 0.05 g of HTC-BSA/GO was completely destroyed in 6 M HNO<sub>3</sub> solution. The BSA concentration in obtained solution was evaluated using standard curve of BSA.

### **2.4. Investigation of BSA release from HTC-BSA/GO**

The studied release mediums were the ethanol-water mixture (volume scale 8/2), 0.1 M NaCl and 0.5 M NaCl solutions. The BSA release from HTC-BSA/GO into the medium was taken by dispersing 1 g of HTC-BSA/GO into 1000 mL of the release medium under stirring. 2 mL of release medium were withdrawn and filtered during immersion time. The BSA amount was monitored by UV–Vis spectroscopy.

### **2.5. Preparation of coatings**

XC35 carbon steel plates with dimension of 15 cm × 10 cm × 0.2 cm were used as substrates. XC35 carbon steel has the composition of 0.35 % carbon, with 0.65 % manganese, and iron to 100 %. Abrasive papers with grade 400 were used to polish the steel surface. The samples were cleaned with ethanol and dried before application of coatings.

The HTC-BSA and HTC-BSA/GO concentration in the coating system were 1 wt.%. They were incorporated in epoxy coatings by magnetic stirring and ultrasonic sonication. The coatings were applied on carbon steel plates by spin coating method. The coatings were cured at ambient condition for 7 days. The measured thickness of dried coatings was  $40 \pm 5$   $\mu\text{m}$ .

### **2.6. Analytical methods**

The FTIR spectra of HTC-BSA and HTC-BSA/GO were acquired on a Nexus 670 Nicolet spectrometer. The XRD spectra of HTC-BSA and HTC-BSA/GO were measured with a Siemens D5000 diffractometer with CuK $\alpha$  target. The UV-Vis absorption spectra were recorded with GBC CINTRA 40 spectrometer. The content of zinc in the collected filtrates containing HTC-BSA/GO was determined by PE 3300 Atomic Absorption Spectrometer.

### **2.7. Test of coatings**

The corrosion resistance of studied coatings was investigated by ASTM B117 salt spray test using Q-FOG CCT-600 chamber. The scratches on the surface of coatings were made by a cutting knife (ISO 17872). The coating samples were exposed in salt fog chamber for 144 h.

The adherence of the coatings system on the steel substrate was measured by pull-off test (ASTM D4541) with a PosiTest AT (DeFelsko). Diameter of the used dollies is 20 mm.

## **3. RESULTS AND DISCUSSION**

### **3.1. Analytical characterization of HTC-BSA/GO**

The BSA loading in the HTC-BSA/GO by using UV-Vis spectroscopy was 19.7 % which is similar to the value of HTC-BSA (21.9 %) [12].

The structure of HTC-BSA and HTC-BSA/GO were analyzed by infrared spectroscopy and X-ray diffraction. Fig. 1 presents the infrared spectra of HTC-BSA and HTC-BSA/GO.

For HTC-BSA, it is observed peaks attributed to Al-O and Zn-O vibration at  $630\text{ cm}^{-1}$  and  $423\text{ cm}^{-1}$ , respectively [15]. Besides, the peaks related to the  $\text{COO}^-$  group of BSA also appear at  $1580\text{ cm}^{-1}$  and  $1423\text{ cm}^{-1}$  [14]. In the case of HTC-BSA/GO it can be seen all peaks characteristic HTC-BSA. Additionally, it is observed characteristic peaks of GO at  $1618\text{ cm}^{-1}$  [16]. These FTIR analysis results demonstrate the presence of GO and BSA in HTC-BSA/GO.

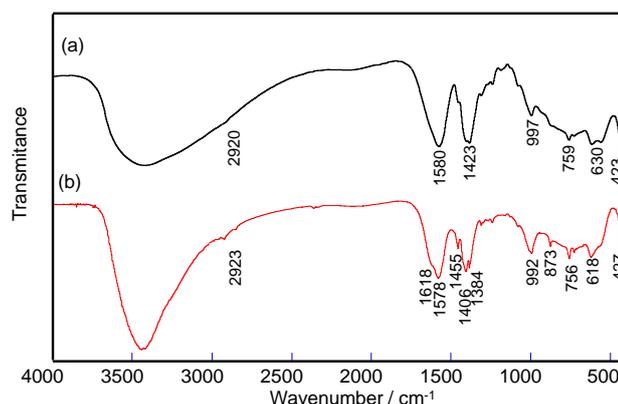


Figure 1. Infrared spectra of HTC-BSA (a) and HTC-BSA/GO (b).

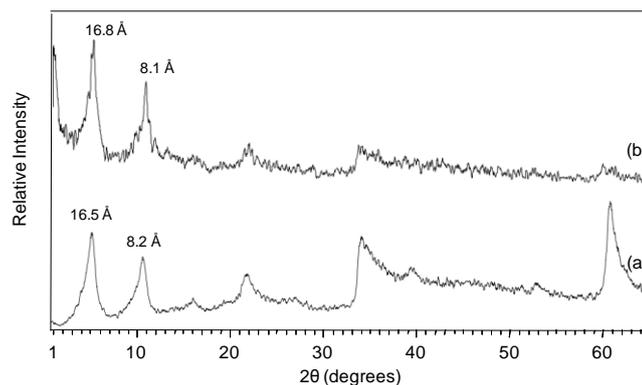


Figure 2. XRD spectra of HTC-BSA (a) and HTC-BSA/GO (b).

The hydrotalcite structure of HTC-BSA and HTC-BSA/GO were evaluated by XRD. Figure 2 presents XRD patterns of HTC-BSA and HTC-BSA/GO. For HTC-BSA, it is observed the typical peaks of HTC structure [15]. HTC-BSA has interlayer distances of  $8.2\text{ \AA}$  and  $16.5\text{ \AA}$ . The interlayer distances of HTC-BTSA are higher than this value of HTC. This indicates the intercalation of BSA in hydrotalcite. In the case of HTC-BSA/GO it can be seen similar diffraction peaks like those of HTC-BSA and the interlayer distances are close to the ones of HTC-BSA. This result shows that the interlayer distance of HTC-BSA/GO did not change very much with the presence of GO.

### 3.2. BSA release of from HTC-BSA/GO

The BSA release from HTC-BSA/GO in NaCl solutions at 0.1 M and 0.5 M concentrations during immersion time was determined by UV-Vis spectroscopy. For comparison the BSA release in ethanol/water mixture was also investigated. The absorbance at  $\lambda_{\max} = 283$  nm was used to calculate the BSA concentration [12]. The Figure 3 presents the BSA release from HTC-BSA/GO in ethanol/water mixture and NaCl solutions at 0.1 M and 0.5 M concentrations during immersion time. It can be seen that for two studied NaCl solutions, the BSA release from HTC-BSA/GO occurred rapidly in the first 8 h of exposure and then the BSA release speed was slow. After 72 h exposure in ethanol-water solution and 0.1 M; 0.5 M NaCl solutions, the BSA release was 6.4 %, 19.3 % and 61.0 %, respectively. The obtained results indicated that the BSA release from HTC-BSA/GO into solutions increased with an increase of the chloride concentrations. The increase of BSA release with chloride concentrations can be explained by the anion exchange between  $\text{Cl}^-$  and BSA intercalated into hydrotalcite. In order to explain the release of BSA from HTC-BSA/GO in ethanol/water mixture without chloride anions, the Zn content into the collected filtrates after 72 h of immersion was determined by Atomic absorption spectroscopy. The Zn content into the collected filtrates was 19.17 ppm. This result indicated that HTC-BSA/GO was partially dissolved, so that BSA was released in the case without chloride anions.

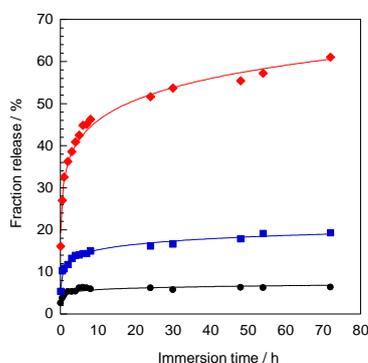


Figure 3. Release of BSA from HTC-BSA/GO versus immersion time in (●) ethanol-water mixture; (■) 0.1 M NaCl solution and (◆) 0.5 M NaCl solution.

### 3.3. Corrosion test of carbon steel covered by free epoxy coatings bearing HTC-BSA/GO Salt fog test

Figure 4 show the photos of coating surfaces after 144 h of salt fog test. It can be observed that corrosion products appear in the scratches on all samples and rust degree of each coating is different. The evaluation of rusting degrees of coatings was performed according to ISO 4628 standard. For blank epoxy coatings, there is more corrosion products in the scratches in comparison to other coatings. In comparison to HTC-BSA, the corrosion degree on the surface of HTC-BSA/GO system is lower. The rust creep from scribe of coatings was calculated. The rust creep from scribe was 1.2 mm; 0.9 mm and 0.7 mm for blank coating, coating loading HTC-BSA and coating with HTC-BSA/GO, respectively. The rust creep from scribe of the blank coating was higher than the one of HTC-BSA and HTC-BSA/GO systems. The lower corrosion degree of samples with HTC-BSA and HTC-BSA/GO by comparison with the bank system can be explained the corrosion inhibition effect of HTC-BSA and HTC-BSA/GO at steel surface [14]. The lower rust creep from scribe for the case of HTC-BSA/GO by comparison with the one of HTC-BSA can be caused by the barrier effect of GO at the scratches. This results is in agreement with the corrosion inhibition effect of HTC-BSA and HTC-BSA/GO. HTC-BSA/GO gives higher inhibition efficiency than HTC-BSA [14]. The obtained results demonstrate that

epoxy coating with HTC-BSA/GO provided higher protection performance than epoxy coatings with HTC-BSA. The presence of GO enhanced the effect of HTC-BSA/GO on protective properties of solvent free epoxy coatings.

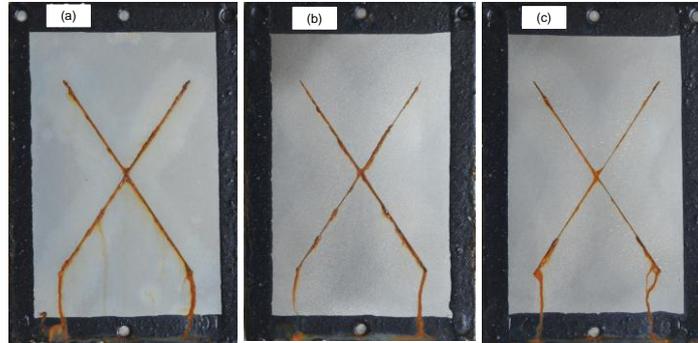


Figure 4. Photographs of samples after 144 h exposure to salt fog test of blank epoxy coating (a), epoxy coating with 1 wt% HTC-BSA (b), and epoxy coating with 1 wt% HTC-BSA/GO (c).

### Adhesion test

The determined pull-off adherence values of coatings are shown in Figure 5. The adherence value of the blank coating, coating with HTC-BSA and coating with HTC-BSA/GO are 2.05 MPa, 2.38 MPa, 2.64 MPa, respectively. Among studied coatings, the coating loading HTC-BSA/GO shows the best adhesion strength. The enhancement of adherence of epoxy coatings with the presence of HTC-BSA and HTC-BSA/GO can be attributed to the reaction of BSA with oxide layer on steel surface [17]. In comparison to HTC-BSA, the adhesion value of HTC-BSA/GO system is higher. The higher adherence obtained with HTC-BSA/GO can be caused by the reaction of carboxylate groups of GO intercalated in HTC-BSA/GO with iron ions on the steel surface. The obtained results show the enhancement effect of GO intercalated in HTC-BSA/GO on the adherence of the solvent free epoxy coating.

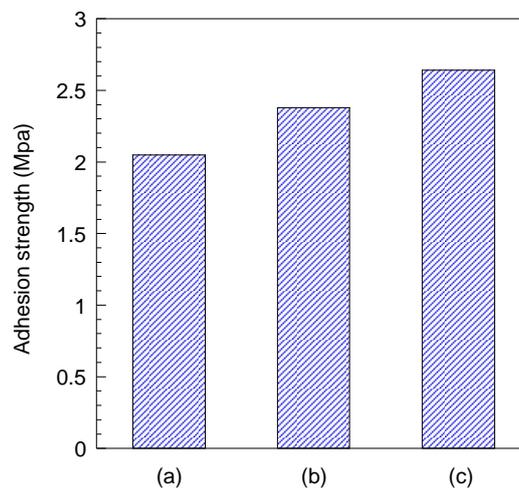


Figure 5. Adhesion value of blank epoxy coating (a), epoxy coating with 1 wt% HTC-BSA (b), and epoxy coating with 1 wt% HTC-BSA/GO (c)

#### 4. CONCLUSIONS

Hydrotalcite loaded 2-benzothiazolylthio-succinic acid and graphene oxide (HTC-BSA/GO) with BSA content of 19.7 wt% was prepared. The BSA release from HTC-BSA/GO depended on chloride concentrations. After 72 h of immersion, the BSA release was 19.3 % and 61.0 % for 0.1 M and 0.5 M NaCl solutions, respectively. The presence of HTC-BSA/GO at 1 wt% improved adhesion and protection properties of solvent free epoxy coatings. The intercalation of GO enhanced the reinforcement effect of HTC-BSA/GO.

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