

Protective Effect on Metal Substrate of Epoxy Resins Containing Corrosion Inhibitor Embedded into Suitable Nanocarriers

FABIANA TESCIONE, MARINO LAVORGNA*,
EUGENIO AMENDOLA and GIOVANNA GIULIANA BUONOCORE

Institute of Polymers, Composites and Biomaterials, National Research Council,
P.le Fermi, 1-80055 Portici, NA, Italy.

*Corresponding author E-mail: marino.lavorgna@cnr.it

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ABSTRACT

The corrosion of metals is a serious technological problem and a variety of methods such as cathodic protection and insulating coatings has been developed to overcome it. However, the use of an *active* coating on metal substrates is proposed to be an innovative and effective approach. Although 2-mercaptobenzothiazole (MBT) is an efficient corrosion inhibitor for metals, its direct addition into the polymer coating or paint is not so much effective, because it is water-soluble, photodegradable and creates discontinuities in the coating layer, thus decreasing its barrier properties. A valuable approach to improve its anticorrosion performance is the entrapment of MBT into nanocarriers. In the present work two different types of nanocarriers have been investigated. In particular, halloysite nanotubes which MBT is loaded in the inner empty lumen through a vacuum procedure, and Zn–Al-layered double hydroxides (LDHs), in which MBT is intercalated through ionic-exchange, have been evaluated. Release tests of MBT from the obtained active particles in aqueous corrosive solution have been performed. Results have been correlated with the data obtained by visual inspection of anticorrosion effect of epoxy coatings used to protect commercial steel substrate during accelerated corrosion tests.

Keywords: 2-mercaptobenzothiazole, Corrosion, Nanocarriers, Active coating.

INTRODUCTION

Corrosion process consists in the deterioration of metal materials through chemical interaction with the external environment. One of the most common strategies used to protect metallic structures against corrosion consists on the application of protective organic coatings. The polymer layers create a barrier and, thus, avoid the contact of water and ion species with the metallic substrate offering a *passive* protection. However the use of coatings suffers from the negative effects of

external agents such as UV radiation, temperature and mechanical action such as the formation of scratches or cracks. These lead to the opening of pores and crack propagation in which water and salts can diffuse and reach the metal interface, ending up in corrosion initiation. In order to prolong the life time of metallic structures, the additional use of an *active* protection is highly desirable. To this aim, corrosion inhibitors can be embedded into the polymeric protective layer^{1,2}. Among them, 2-mercaptobenzothiazole (MBT) is one of the most widely used corrosion inhibitors for many metals³ in

applications fields such as aeronautic, automotive and ship building industries. However, it is well known that MBT can be photodegraded by solar irradiation and it can be critical for the corrosion protection⁴. Further more the inhibitors are prone to leach from the polymer layer thus leading to rapid exhaustion of their anti-corrosion activity. To overcome these drawbacks, a valid approach is represented by the designing of *active* coatings wherein the inhibitors are encapsulated in micro/nano carriers⁵. In this coatings the nanoparticles act as a reservoir and allow the slow release over time of the inhibitor.

In the present paper the effect of epoxy resins loaded with 2-mercaptobenzothiazole embedded into two different types of nanocarriers on the corrosion protection of commercial steel substrates has been investigated. The two nanocarriers are halloysite nanotubes (HNTs) and Zn-Al-layered double hydroxides (LDH). Halloysite is a naturally mineral clay normally described as a gibbsite octahedral sheet ($\text{Al}(\text{OH})_3$), which is modified by siloxane groups at the outer surface, and has a 1:1 Al:Si ratio and stoichiometry $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ ⁶. The size of halloysite tubes varies from 500-1000 nm in length and 15-100 nm in inner diameter⁶. Halloysite exhibits a range of morphologies, and its structure depends on crystallization conditions and geological occurrences⁷. Halloysite nanotubes are attractive materials due to their availability, relatively low cost and wide range of applications. It has been used as support for immobilization of catalysts such as metal-complexes⁸⁻¹¹ and for the controlled release of anti-corrosion agents, herbicides and fungicides¹²⁻¹⁷. Herein, with the aim to control the release of the anticorrosion agent, we propose to modify the anticorrosion filled HNT particles with a chemical cross-linker, such as copper ions, able to produce a network acting as a physical ending stopper¹²⁻¹⁶.

Layered double hydroxides (LDHs general formula of $\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2(\text{A}^n)_{n/x} \cdot m\text{H}_2\text{O}$), also sometimes termed anionic or hydrotalcite clays are a class of layered materials consisting of positively charged brucite-like layers and the charge compensating interlayer exchangeable anions¹⁸. Synthesis and chemical modification of LDHs offer attractive research opportunities, mostly due to their good environmental stability and simple

intercalation/deintercalation chemistry. Tremendous potential applications of LDHs in catalysis, medicinal materials, waste removal, polymer nanocomposite, and drug delivery have already been reported^{18,19}.

The ability of LDH to act as a generic anion delivery system leads to the possibility to immobilize organic anion inhibitors by intercalation between hydroxide layers. Herein two LDHs, characterized by different morphology, i.e. LDH rose and flat particles have been used to embed the MBT corrosion inhibitor. They differ from the dimension of particles, in particular the LDHs with the rose morphology, range from 600 to 1500nm, while the LDHs with the flat morphology, range from 8000 to 15000nm. Furthermore, the first appear as aqueous wet powders, whereas LDH flat are dry powders.

The MBT-loaded HNTs and LDH particles were characterized using Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis. The MBT release kinetics from the loaded nanoparticles were investigated using UV-vis spectroscopy and the obtained data were correlated with the protective effect of MBT-containing resins on metallic substrates which has been studied by visual observation during accelerated corrosion tests.

MATERIALS AND METHOD

Materials

Halloysite nanotubes were provided from Imerys Ceramics (UK). Zinc-aluminum 2-mercaptobenzothiazole hexahydrates 'rose wet powders' ($[\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2](\text{MBT})_{0.33} \cdot 2,4 \text{H}_2\text{O}$) and Zinc-aluminum 2-mercaptobenzothiazole hexahydrates 'flat dry powders' ($[\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2](\text{MBT})_{0.3}(\text{CO}_3)_{0.015} \cdot 2,9 \text{H}_2\text{O}$), were purchased from Prolabin&Tefarms.r.l. (Perugia, Italy). A commercial ferritic steel was used as substrate material for the coating. The 2-mercaptobenzothiazole, used as the corrosion inhibitor and sodium chloride, used for corrosion studies were purchased from Sigma-Aldrich (Italy). The polymeric coating was obtained by using a liquid epoxy resin (DGEBA, provided from ELANTAS Camattini S.p.A.) cured with Jeffamine D230 (Sigma Aldrich, Italy), a poly propylene glycol bis-2-aminopropyl ether used as hardener. All the chemicals were used as received.

Experimental section

Procedure for loading of MBT in HNT nanotubes

HNT powders were sieved using a 63µm mesh and then dried at 120°C overnight to remove adsorbed water. Afterwards, the HNTs were firstly treated under vacuum for 24h to remove the air entrapped in the lumens and then mixed with the saturated MBT solution in acetone in order to load the corrosion inhibitor. After 30min, the vial was taken from the vacuum jar and the suspension was brought in an ultrasonic bath, at room temperature for few minutes to avoid the aggregation of HNT and improve their dispersion in the saturated solution. The vial containing nanotubes and MBT solution was placed in a jar and kept under vacuum for 30min. Then the suspension was recovered and kept under stirring for 30min. This process was repeated three times to increase the loading efficiency. The MBT-loaded HNTs were separated by centrifugation (4000 rpm for 3 min), rinsed rapidly with water to remove the free MBT and dried via oven at 60°C overnight.

It has been reported that to avoid burst release and to prolong the release time of organic molecules from HNT lumen, it is possible to form a complex between the active molecule loaded in HNTs and copper ions (Cu^{2+})^{8-11, 14, 10}, which contribute to form a network that acting as physical stopper. The MBT cross-linking was realized by treating the loaded nanotubes with a copper ions solution which, diffusing into the tube openings, formed an insoluble metal-MBT complex capping the tube ends²⁰. For this purpose, MBT-HNT particles were exposed for 1 min to the bulk aqueous solution containing copper ions (CuSO_4) under continuous stirring. The obtained nanotubes, coded MBT-Cu-HNT, were separated from the solution by centrifugation and dried in oven at 60°C overnight.

Preparation of the active epoxy coating

The production of epoxy-based coatings has been obtained by using the Thinky instrument, to remove the air entrapped in the mixtures, following the three cycles reported in Table 1. Jeffamine D230 was added to the homogeneous systems in stoichiometric amount with respect to the epoxy groups present in the resin, and the same Thinky cycles were applied two times. Active epoxy-based coatings were prepared by adding suitable

amounts of MBT-loaded nanocarriers in order to obtain in all the films an MBT amount equal to 1% w/w with respect to epoxy weight.

The mixtures were deposited on the surface of the commercial steel substrates through Elcometer Film Applicator, using a thickness of 30 microns. Finally, epoxy-based coatings were cured in the oven at 170°C for 15 minutes. A pristine epoxy coating was also prepared as control sample.

The following samples were prepared: pristine epoxy coating (labelled as DGEBA+D230); coating filled with MBT_HNT (labelled as DGEBA+D230+MBT_HNT); coating filled with MBT_Cu_HNT (labelled as DGEBA+D230+MBT_Cu_HNT); coating filled with MBT_LDHe (labelled as DGEBA+D230+MBT_LDHe) and finally coating filled with MBT_LDHe (labelled as DGEBA+D230+MBT_LDHe).

Preparation of metal substrate surfaces

A commercial ferritic steel sheet was cut into rectangular specimens (8.5 x 5.5 x 0.2 cm³), abraded with silicon carbide (SiC) emery sheet up to 1000 grit, cleaned with sodium hydroxide solution (0.1M), deionized water, and finally in ethanol to remove oil and dust. Then, the substrates were coated using the different epoxy-based coatings.

Characterization

The morphology and structure of the inorganic carriers were investigated using Scanning electron microscopy (SEM), a Leica model S440 (Leica Microsystems GmbH, Germany) operating at 20 kV. The powders were placed on the support and coated with gold with a sputter coater (Emscope SC500, UK) before they were observed under the microscope.

Active nanoparticles were characterized by infrared spectroscopy analysis and thermogravimetric analysis. FT-IR spectra were collected with a Nicolet FT-IR spectrophotometer using a KBr pellet over a range of 4000–400 cm⁻¹ with a resolution of 2 cm⁻¹. The thermogravimetric analysis (TGA) was performed by using a TGA 500 (TA Instruments), submitting the samples to a heating run from 30°C up to 900°C at a heating rate of 10°C/min, under nitrogen flux.

The release kinetics were determined by mixing the MBT-loaded nanocarriers powder in corrosive solution ($[\text{NaCl}] = 0.05\text{M}$) at $\text{pH}=7$ at room temperature and sampling the solution at prefixed time intervals. The amount of released 2-mercaptobenzothiazole as a function of time was monitored by UV Vis analysis by using a Agilent Technologies Cary 60 UV Vis spectrophotometer at absorption intensity peak at ca. 322nm. A calibration curve of MBT was obtained by plotting the absorbance vs. MBT concentration between 1 and 10ppm.

Accelerated anticorrosion studies were performed by scratching the polymer coating with a cross cut, thus exposing the uncoated surface of steel substrate to corrosive conditions. The scratched coated substrate was dipped into corrosive solution ($[\text{NaCl}] = 0.05\text{M}$) for 1 minute every day, and kept in a closed chamber containing a saturated solution of NaCl. Trough visual observation it has been

possible to evaluate the time needed to visualize the occurrence of corrosion spots and their extension and amount.

RESULTS AND DISCUSSION

Figure 1 shows SEM/TEM images for pristine nanocarriers. HNTs particles possessed a typical hollow tubular structure and both ends were open. The internal and external diameters of the HNTs ranged from 15 to 30nm and 30–100nm, respectively. The SEM micrograph reported in the Figure 2(left side) shows LDH submicron particles aggregated to form the rose morphology sized between 600-1500 nm. Whereas in Figure 2(right side) is showed the hydrotalcite particles with a flat morphology, with a hexagonal shape and size between 8-15 μm .

Figure 3 displays the FTIR spectra of HNTs samples before and after loading procedure with MBT. Compared to the unloaded sample, MBT-HNT and MBT-Cu-HNT samples exhibit some new FTIR peaks, such as several peaks around 1496cm^{-1} attributed to the benzene ring stretching, the $\text{C}=\text{N}$ stretching at 1322cm^{-1} , typical of the MBT spectra, and the $\text{C}-\text{C}-\text{C}$ bending absorption band at 1011cm^{-1} .

Table1: Thinky cycles

Speed	2000 rpm	600 rpm	2000 rpm
Vacuum	yes	no	yes
Time	2min	4min	4min

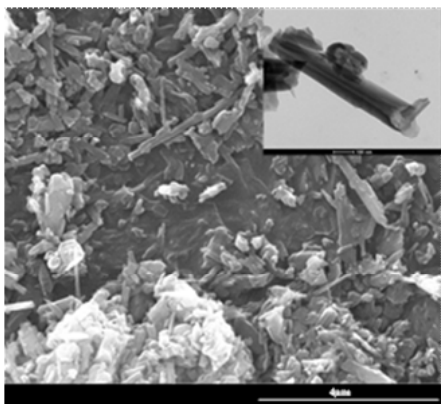


Fig. 1: SEM and TEM images of raw HNTs

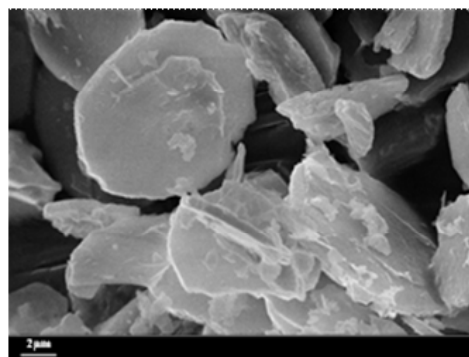
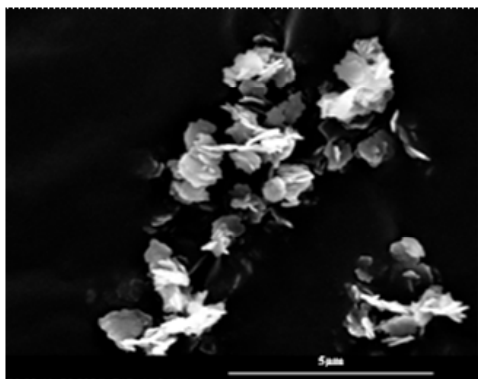


Fig. 2: SEM of two hydrotalcite particles, on the left shown LDH rose and on the right the flat type as courtesy by Prolabin & Tefarm

The infrared spectrum of the LDH systems were shown in Figure 4. The LDH characteristic infrared absorption bands were observed at around 3500cm^{-1} , likely ascribed to the brucite-like layer (OH stretching vibration), at 1623cm^{-1} due to the hydroxyl stretching and at 1384cm^{-1} due to NO_3^- . In the spectra of the loaded nanocarriers, it is possible to identify the MBT bands at 3000cm^{-1} due to the C-H deformation, the C=N stretching at 1322cm^{-1} , and the C-C-C bending absorption band at 1011cm^{-1} .

MBT loading efficiency was determined by thermogravimetric analysis. In Figure 5 the TGA diagrams of HNT, pristine MBT and the two MBT-loaded Halloysite nanocarriers have been reported. The MBT curve shows only one weight loss which is

completed at about 275°C . HNT curve exhibits one degradation step at about 500°C which is attributed to the dehydroxylation of the matrix²². By comparing the weight loss of the loaded halloysite with that of an unloaded sample, it is possible to calculate the loading efficiency by taking into account the difference of residue at 800°C . The obtained data show a load efficiency equal to about 10% w/w for both nanocarriers. The results also confirm that in the case of HNT the loading efficiency does not change after Cu^{2+} solution treatment.

TGA curves of pristine MBT and LDH systems are shown in Figure 6. As mentioned above, the MBT curve shows only one weight loss which is completed at about 275°C . In the case of MBT-

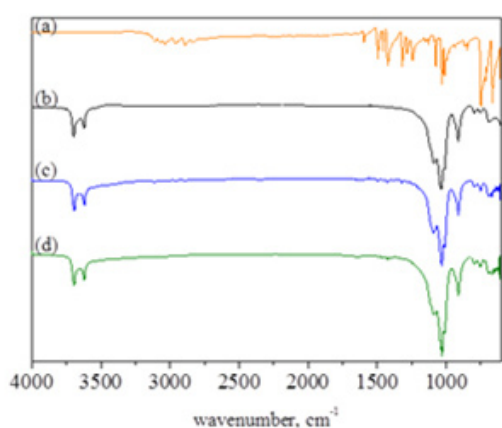


Fig. 3: FT-IR spectra: (a) MBT, (b) HNT, (c) MBT-HNT and (d) MBT-Cu-HNT

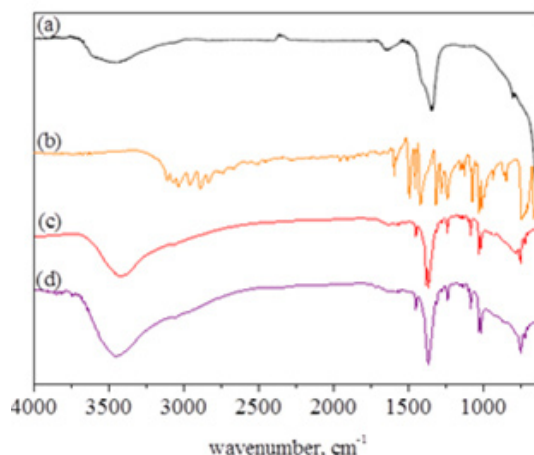


Fig. 4: FT-IR spectra: (a) LDH- NO_3^- , (b) MBT, (c) MBT-LDHr and (d) MBT-LDHf

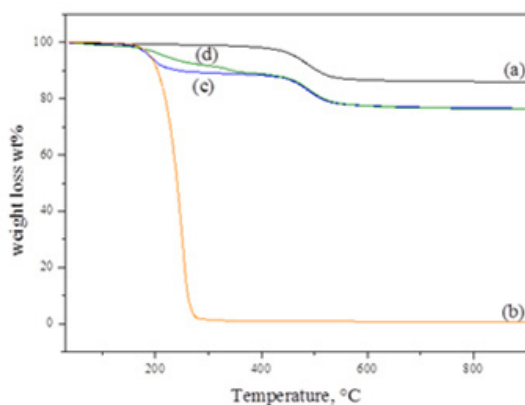


Fig. 5: Weight loss (wt%) of (a) HNT, (b) MBT, (c) MBT-HNT and (d) MBT-Cu-HNT

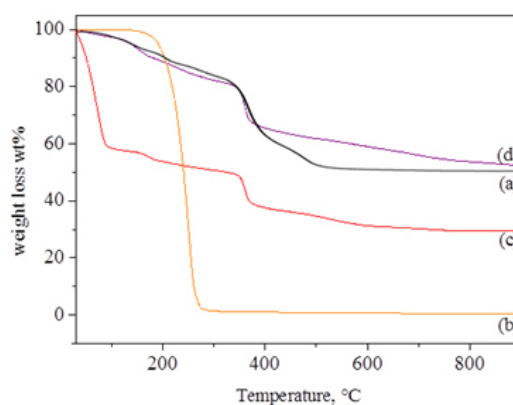


Fig. 6: Weight loss (wt%) analysis on (a) ZnAl-LDH, (b) MBT, (c) MBT-LDHr and (d) MBT-LDHf

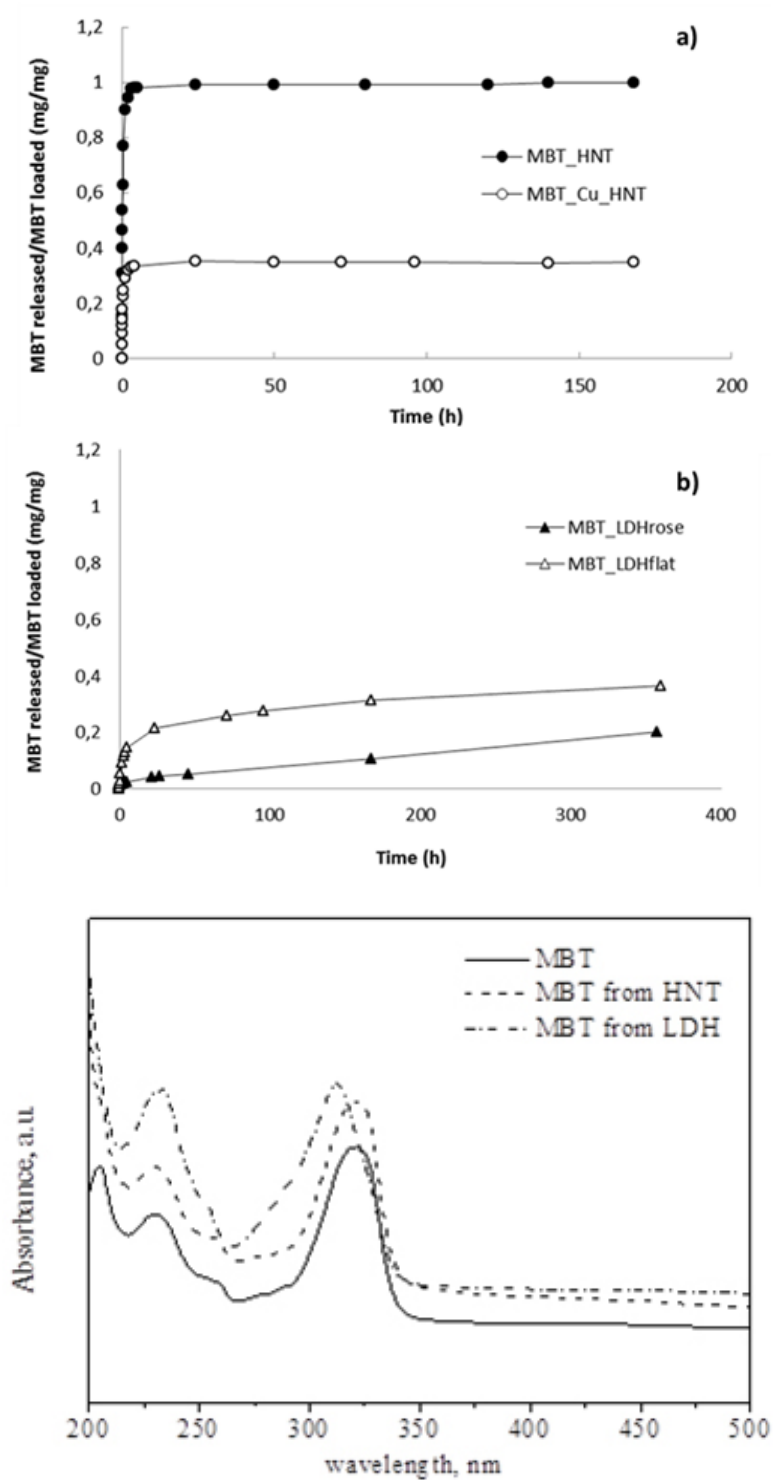


Fig. 7: Release kinetics of MBT from neat and complexed HNTs (a) and from rose and flat LDH (b). (c) MBT UV spectra from different nanocarriers

LDHr particles (wet state), three thermal degradation steps can be observed: the first step is related to water evaporation; the second one between 100 and 180°C is due to the loss of interlayer hydrogen bonded water molecules; the third step corresponds to the overlapping of layer de-hydroxylation and to the decomposition of intercalated anion.

The amount of MBT released from the active nanoparticles in corrosive NaCl solution (0.05M, pH=7) at 25°C was monitored as a function

of time. In Figure 7a and 7b, release profiles of MBT from pristine and complexed halloysite nanotubes, and from rose and flat LDHs were respectively reported.

From Figure 7a it can be inferred that the release of MBT from the active HNT nanoparticles takes place very quickly within 5 hours and can be considered complete in 24 hours. Also in the case of HNTs loaded with MBT and treated with copper solution, the complete release of MBT is very fast

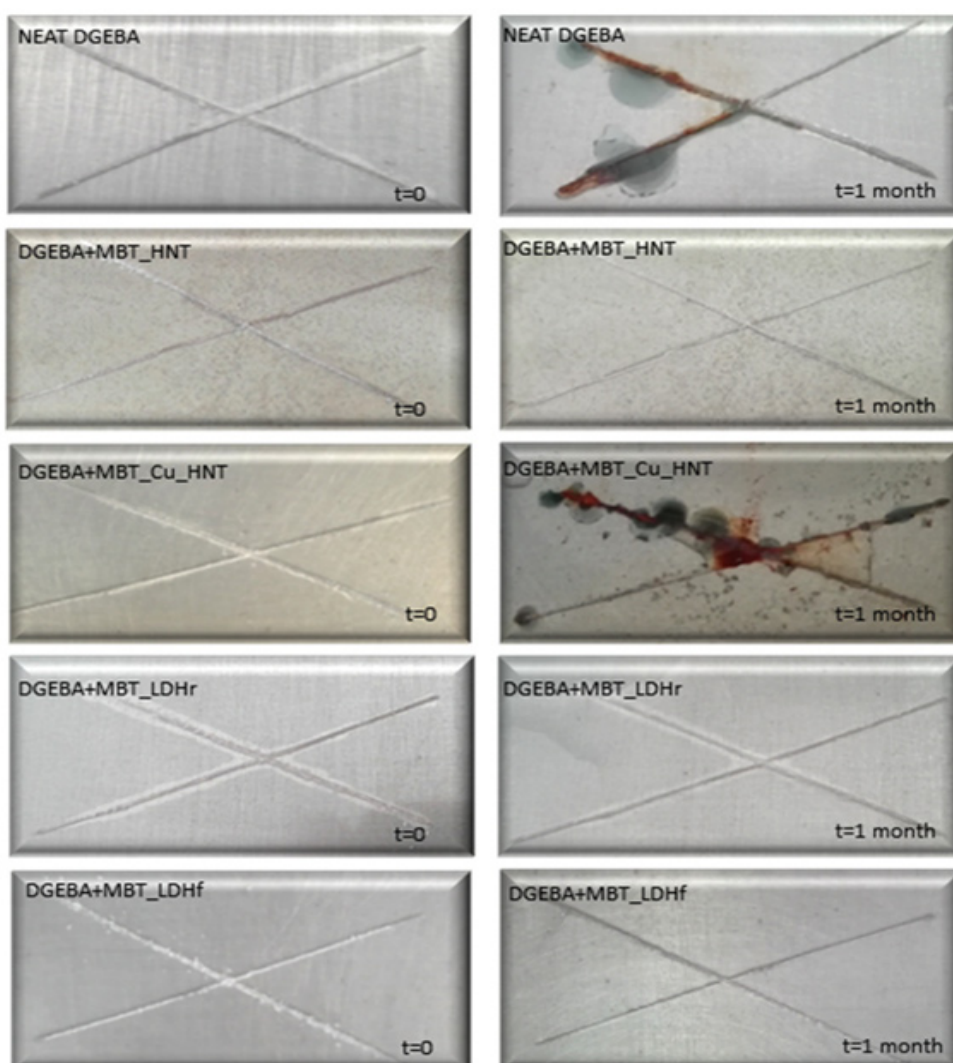


Fig. 8: Pictures of the scratched steel substrates coated with the various epoxy resins after 0 days (left) and 30 days (right) of contact with the corrosive NaCl solution. (a) DGEBA+D230, (b) DGEBA+D230+MBT_HNT, (c) DGEBA+D230+MBT_Cu_HNT (d) DGEBA+D230+MBT_LDHr and (e) DGEBA+D230+MBT_LDHf

and is completed after 24 h. However, the amount of inhibitor released at the equilibrium (34%w/w) is less than that initially loaded into the particles. This can be likely ascribed to a very stable complex formed between MBT and Cu ions¹⁴, which prevents the total release in the surrounding aqueous medium.

As for LDH nanocarriers, it is worth noting that the mechanism of MBT release is related to the ion-exchange capacities in the chloride-based aggressive environment. From Figure 7b, it can be noticed that, after 15 days, MBT release from both rose and flat LDHs has not reached the asymptotic value and that MBT anions are released to a higher extent from the LDH flat nanocarrier with respect to the amount released from LDH rose system. Since LDH flat consists in a dry powder where as the LDH rose are wet particles, this different releasing behavior can be ascribed to the presence of electrostatic interactions between MBT ions and water molecules, which increase the MBT stability in the LDH rose carrier, thus decreasing the released amount.

Figure 7c shows the UV-vis spectra of pristine MBT and MBT compound released respectively from HNT and LDH systems. It's observed that the spectrum of MBT from HNTs is comparable to that of pristine one. In contrast the spectrum of MBT released from LDHs systems is somewhat different. This difference may be tentatively ascribed to the presence of anionic MBT compounds which are embedded in the LDHs structures.

Anticorrosive effect of MBT during accelerated corrosion process of metallic substrates was studied by visual observation of corrosion spots in the scratched area of the steel substrate coated with epoxy resin. In Figure 8 the optical photographs of the scratched steel substrates coated with neat and active epoxy resins, at time zero and after 30 days of contact with corrosion solution, are reported.

Pictures show that pristine epoxy-based coating, not containing the corrosion inhibitor, is not able to protect the metallic substrates from the corrosion process which rapidly and extensively occurs (Fig. 8a), after one day aging. In the case

of DGEBA+D230+MBT_HNT resin (Fig. 8b), the presence of MBT absolutely hinders the corrosion process up to 30 days of exposure to corrosive solution. Whereas, when MBT is embedded into HNTs treated with copper solutions, the corresponding active coating is not effective in protecting the scratched coated substrate from corrosion (Fig. 8c). This behavior is supported by the release data which show that MBT forms a stable complex with Cu ions and thus it is not available to be released (only 40%w/w of loaded MBT is released). It's likely that the released MBT amount is not enough to establish a protective coating in the scratched zone. On the other hand, interesting results are reported when the metal substrate is coated with resins containing MBT-loaded LDHs. Figure 8d) and 8e) show no visible degree of corrosion up to 30 days of exposure. In this case, even if the release of the active compound is not complete, the released anionic MBT (as confirmed by UV spectra) is very effective to prevent corrosion process even at low concentrations. As previously reported, LDH are anion-exchange compounds and the anticorrosive MBT anions can be exchanged by the corrosion-active ions such as chlorides present in the aggressive environment. In this case, the high performance in corrosion protection is mainly due to the twofold action of the LDH nanostructured epoxy-based coating which steadily releases the effective active MBT anions compound over exposure time and also provides a good barrier to the penetration of corrosive and aggressive species.

CONCLUSIONS

The preliminary results reported in this paper confirm that the designing and preparation of active coating is a valuable approach to contrast the mechanism of corrosion of metal substrate and may ensure a long-term stability of the metallic objects. It has been shown that the coatings based on LDH particles loaded with anionic anticorrosion inhibitors MBT are more effective in protecting the metallic substrate with respect to the coating based on HNT particles filled with MBT. The different behavior is ascribed to both the different releasing mechanisms and the different released species. In fact in the case of HNT particles, the inhibitor is quickly released as neutral MBT specie in the aqueous solution and, thus, it shows a stabilization

effect of the metal substrate. On the other hand, the results obtained for the coatings containing MBT loaded into copper-treated HNT particles confirm that when the MBT is released at lower concentration is not able to promote the formation of a stable anticorrosion layer. In the case of LDHs, the anionic form of the inhibitor is slowly released from the particles, because that depends on the ion exchange process, thus providing steadily new anticorrosive molecules which result more effective in contrasting the process corrosion.

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