



Xuejun Zhang, Benjamin P. Pearman, Jeff W. Buhrow, Lilliana Fitzpatrick, Wenyan Li, Jan M. Surma,  
Eliza L. Montgomery and Luz M. Calle

NASA, Kennedy Space Center  
Corrosion Technology Laboratory  
Kennedy Space Center, FL, 32899  
USA

## ABSTRACT

Novel inorganic carriers have been developed for the controlled release of corrosion inhibitors in corrosion protective coatings. These carriers are being designed to detect and respond to the external and internal changes that may initiate a corrosive process or that result from the initiation of the corrosive process itself. The formation of complexes between the inhibitor and the inorganic framework gives this delivery system the ability to respond to pH and temperature changes by delivering the encapsulated corrosion inhibitor(s). These inorganic particles possess a hierarchical architecture that can recycle superfluous active compounds by absorbing them back into their framework. Release studies and corrosion tests confirmed the immediate, as well as prolonged release, properties of these particles. These multi-stimuli controlled release particles were incorporated into coating systems to test their effectiveness. Salt fog testing showed that these smart inorganic carriers, when incorporated into coating systems, significantly improve the corrosion protection of carbon steel and aluminum substrates.

Key words: encapsulation, inorganic carriers, smart particles, controlled-release, corrosion, corrosion inhibitors

## INTRODUCTION

The concept of stimuli responsive carriers for controlled on-demand delivery of corrosion inhibitors has generated a great deal of interest in the corrosion control field. Many researchers are developing novel smart corrosion protective coatings by incorporating these systems into coating formulations.<sup>1</sup> The corrosion protection function of these coatings is enabled by the smart carriers, which are able to release the encapsulated content in response to the local changes associated with corrosion. These smart carriers may be triggered on and off by various internal or external stimuli, which often accompany the metal corrosion process, such as: variation of the pH and temperature, redox reactions, and changes in the ionic strength.<sup>2</sup>

A broad range of pH-stimuli carriers, such as microcapsules and micro-particles, with appropriate sizes, composition, structure and properties have been designed to encapsulate various corrosion protecting agents. Microcapsules, synthesized from organic polymers, have been used to encapsulate corrosion inhibitors or self-healing compounds by water-in-oil and oil-in-water micro-emulsion polymerization. Examples of the polymers that have been used include: resorcinol formaldehyde (RF), melamine formaldehyde (MF), urea formaldehyde (UF), melamine-resorcinol-formaldehyde (MRF), resorcinol-modified poly(urea-formaldehyde) (PUF), and functionalized forms of these polymers.<sup>3-9</sup> Organic polymer carriers are suitable to encapsulate most nonionic inhibitors but can have limitations, such as a low loading capacity, and are not the best choice for encapsulating highly water-soluble or ionic corrosion

inhibitors. These inhibitors are more likely to leach out when incorporated into a coating and cause blisters. Inorganic-based frameworks such as silica,<sup>10-14</sup> zirconia,<sup>15</sup> other metal oxides,<sup>16</sup> zeolite,<sup>17</sup> and organic inorganic hybrids<sup>18-21</sup> have also been used as inhibitor carriers for controlled on-demand release purposes. One way to obtain an inorganic on-demand release system as a host carrier is to simply imbue anticorrosive compounds into a pre-made porous framework or carrier. However, due to the lack of a strong interaction between the loaded compounds and carrier materials, these carriers are likely prone to leaching, thus limiting their use to deliver low solubility compounds. The controlled delivery of active content from submicron or nano-sized carriers is seldom achieved with a simple architecture. Therefore, organic and inorganic hybrids or composites are often considered to design multifunctional carriers. Inorganic nano-containers, coated with polyelectrolyte shells, using a layer-by-layer (LBL), technique have been developed.<sup>22-24</sup> An important advantage of these systems, when compared to the pure organic or inorganic containers, is their better coating compatibility and lower tendency to leach. However, their synthesis is a somewhat complicated process involving multiple steps, such as preparation of porous silica particles, adsorption of active compounds under reduced pressure, and the formation of multiple layers around the silica particles. This process can be expensive, time consuming, and difficult to scale up, which are limiting factors for future industrial applications. Given that currently available carriers for corrosion protection are mostly single stimulus responsive, several challenges remain in designing a non-leaching multi-stimuli delivery system in aqueous solvent for inhibitors with high water solubility. These challenges can be overcome with a new encapsulation strategy that has the following features: i) increased interaction between carrier and inhibitors for high loading capacity without leaching; ii) additional functionality for multi-stimuli-responsiveness; and iii) a feasible, universal, cost effective, easily scalable, and environmentally friendly synthesis method.

In this paper, we report the first *in-situ* method for immobilizing ionic corrosion inhibitors in an aqueous solution, under mild reaction conditions. This method has been used successfully to encapsulate a broad range of water soluble corrosion inhibitors into silica carriers. The authors have developed a smart, dual pH- and thermally controlled release system, to encapsulate and release corrosion inhibitors for corrosion protection. The dual stimuli responsiveness is of great importance for realizing more efficient inhibitor release. This work also shows one of the first examples of pH- and thermally controlled release of an ionic corrosion-inhibiting compound, sodium 2-mercaptobenzothiazole (NaMBT). While there is a large variety of organic corrosion inhibitors, 2-mercaptobenzothiazole (2-MBT or MBT) has been a major focus of research among corrosion scientists due to its interesting structural and unique properties. 2-MBT is a heterocyclic thioamide with two tautomeric forms, thiol and thione, which can potentially split into bidentate ligands with multiple electron donor sites. The thiol form can deprotonate to generate the anionic MBT<sup>-</sup>, which is a negatively charged bidentate ligand with nitrogen (N) and sulfur (S) donors. A great deal of information is available about 2-MBT and its low water solubility, thus making it suitable to be encapsulated into polymeric frameworks. Less information is available in the literature about anionic MBT<sup>-</sup>, which is highly soluble in water, and has never been encapsulated into any on-demand controlled-release systems. The authors have developed a delivery system for anionic MBT. These delivery containers were incorporated into epoxy and waterborne coatings in order to evaluate the corrosion protection effectiveness of the encapsulated sodium NaMBT.

## EXPERIMENTAL PROCEDURE

**Materials:** The following chemicals were purchased from Sigma-Aldrich: NaMBT, tetramethyl orthosilicate, cetyltrimethylammonium bromide (CTAB), methyl isobutyl ketone, acetone, polystyrene monohydroxyl terminated MW 10 000 (PS 10,000), and toluene.

**Synthesis of controlled release particles:** Three different controlled release particles were prepared following procedures previously disclosed:<sup>25</sup> A particle, labeled as CMBT, formed by reacting NaMBT

with CTAB in aqueous solution; a particle, labeled as SiNaMBT, obtained by adding tetramethyl orthosilicate to a CMBT suspension to encapsulate the CMBT particle in silica; and a hybrid particle, labeled as SiPSNaMBT, obtained by reacting CMBT with polystyrene (PS) 10,000 and tetramethyl orthosilicate. This particle consists of a CMBT core covered with a layer of PS and a silica layer on the outside. All three particles were separated, washed and dispersed into deionized (DI) water and dried using a spray dryer (Pulvis Mini Spray, GS 310, Yamato<sup>†</sup>).

*Preparation and Testing of epoxy coated Al2024 panels:* Al 2024 T3 bare panels, cleaned with acetone, were used as metal substrates. An epoxy model coating, with low epoxy blend and blocked polymeric isocyanate hardener, without pigment, was used as control coating. Both SiNaMBT and SiPSNaMBT particles were added to the control at 5% (wt/vol) loading. The coating was applied to aluminum panels, using a wire draw bar, resulting in approximately 3.6 mils of wet film thickness. The coated panels were cured at 170°C for 20 minutes after air drying for 24 hours. The coated panels were scribed with a single center-aligned vertical scribe using a generic scribing tool. The uncoated back and edges of the coated panels were taped before the panels were tested in a salt fog chamber following ASTM B117 standard.<sup>26</sup>

*pH Controlled-Release study:* 20 mg of the aforementioned microparticles, containing NaMBT, were dispersed in 20 ml of 0.01 M KOH at a concentration of 1000 mg of particles/g of solution and continually stirred at 300 rpm. Aliquots of samples were taken after 1 hour, 24 hours, 1 week, 2 weeks, 4 weeks and then every 4 weeks until no further release was observed. The samples were filtered through a 0.2 µm nylon filter and appropriately diluted. The concentration of the NaMBT was measured using HPLC-AES.

*Infra-red (IR) reactor study:* A monitoring method for the quantitative simultaneous determination of solid phase in solution was developed using an IR reactor. IR measurements were done on a Mettler Toledo ReactIR 15 reactor<sup>†</sup>. Mettler Toledo Optimax 1001<sup>†</sup> Analyst software was used to control the reactor. The ReactIR<sup>™</sup> *in situ* probes were used as an *in situ* reaction monitoring tool for recording the turbidity, temperature, and pH values of the mixtures. An IR probe with a PbSe rod crystal was used to obtain the IR spectra. The reactions were carried out in a 1000 ml glass flask kept under constant stirring (600 rpm) and were started at a temperature of 25 ± 1 °C.

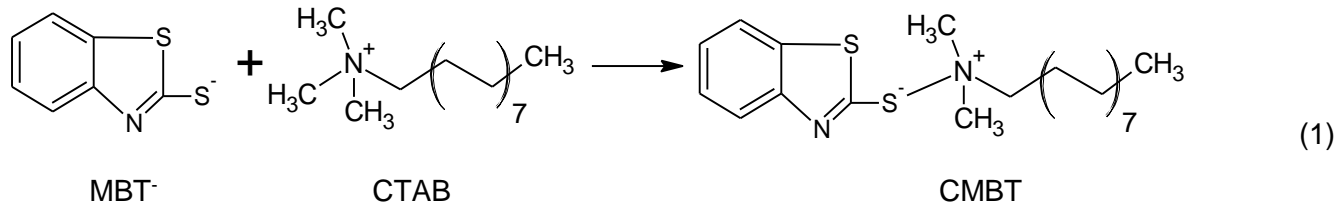
*Characterization:* The structure of the particles was observed by scanning electron microscopy (SEM) using a JEOL JSM-7500F<sup>†</sup>. All samples were first dispersed into deionized (DI) water, heated to 70°C, deposited onto heated stubs without tapes and coating, and allowed to cool down to room temperature before analysis. The mean diameter and size distribution of the particles were obtained from the statistical data for 100 particles from SEM images, analyzed using Image-Pro Plus 6.0.<sup>†</sup> The thermal properties of the samples were characterized by thermal gravimetric analysis (TGA, Q5000, TA Instruments<sup>†</sup>) and differential scanning calorimetry (DSC, Q2000, TA Instruments<sup>†</sup>). The chemical composition of the particles were determined by Fourier trans-infrared spectroscopy (FT-IR, Bruker, Alpha<sup>†</sup>) on an instrument equipped with an attenuated total reflectance (ATR) accessory. Observations were made in the 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> range of the spectrum. FT-IR samples were prepared by mixing a small amount of particles with potassium bromide (KBr) and then compressing them into tablets for analysis. The particle samples were spray dried.

*Accelerated corrosion testing:* Testing of the coated panels was carried out in a QFOG CCT-1100 salt fog chamber (Q-Labs) following ASTM B117<sup>26</sup>. Panels were placed in the chamber and removed after 500 hours of continuous testing for evaluation.

## RESULTS AND DISCUSSION

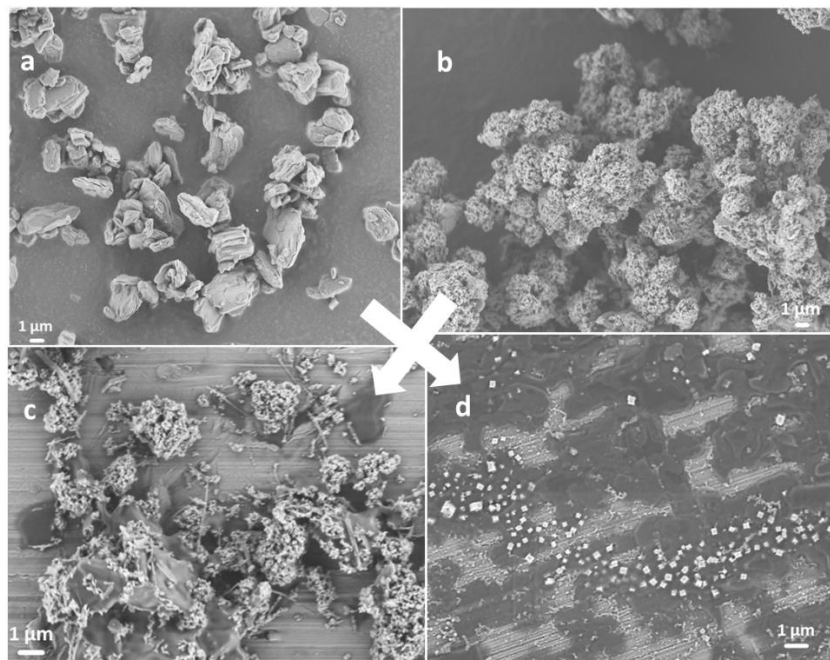
The synthesis procedure for the controlled-release inorganic containers includes two main steps. An initial solid complex, CMBT, is prepared by dissolving the water-soluble corrosion inhibitive compound,

NaMBT, into an aqueous solvent, followed by the addition of a counter ionic surfactant, CTAB, to form the pH-/thermal-sensitive cores. Subsequently, CMBT is encapsulated into silica through a sol-gel process to form the inorganic carriers. The proposed reaction for the formation of the initial complex is shown in Figure 1.



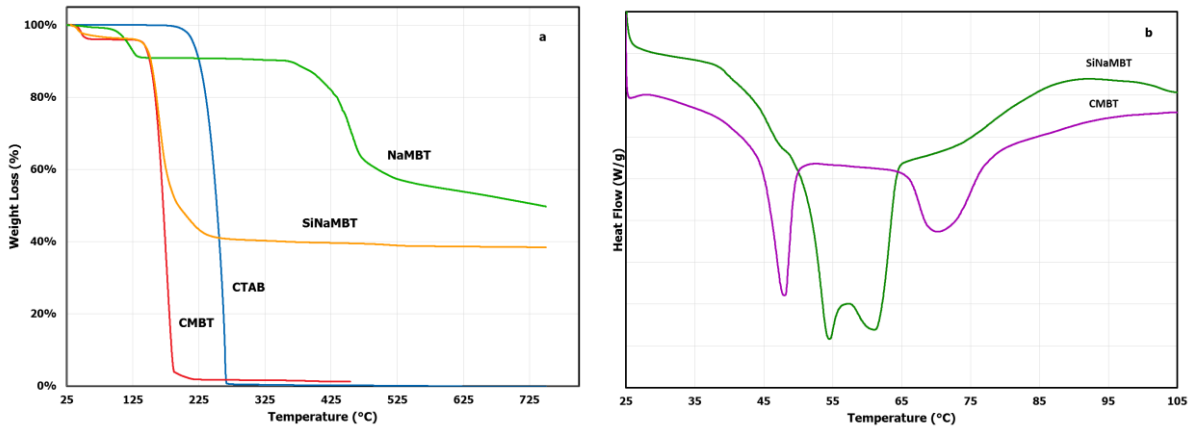
The formation of the initial complex is advantageous in that it allows the very water soluble inhibitor, NaMBT, to be immobilized by CTAB and subsequently self-assembled into micro-/mesostructured micelles. The inorganic sol-gel precursor directly co-assembles with the initial core to form a porous inorganic framework. The CMBT embedded in the metal oxide matrix can be mobilized under alkaline and/or acidic conditions, which enhances the pH-controlled release function, as well as the time-release mechanism, of the inorganic particles. The initial core of CMBT is thermally sensitive as well. This provides both pH and temperature dual-stimuli-responsive controlled release functionality. When above a certain critical temperature and below or over a certain pH value, the bound active compound can be mobilized by thermo-stimuli release as well as pH-controlled release. This strategy can also be applied to other ionic inhibitors.<sup>25</sup>

The design of the smart controlled-release carriers is often determined by their applications. For corrosion inhibitor delivery, the inhibitor loading levels and release kinetics are directly affected by the size of the carriers. Carriers of submicron size are preferable for thin coating applications and where quick inhibitor response is needed. The interaction between the content and the shell of the carriers play an important role during development of nano-/microscale systems for targeted active agents. In fact, the controlled release can be achieved by not only the functionality of the carrier but also the entrapment of inhibitors. More often than not, the inhibitors are entrapped in the carrier “chemically” instead of “physically”. That is, the carrier is not only acting as a container but also interacting with the inhibitors. Sometimes, complexes are formed between inhibitors and carriers through a non-covalent bond type of interaction, such as hydrogen bonds, electrostatic attractions, Van der Waals forces, Coulomb forces, “salt” linkages or other attractive interaction to achieve the controlled-release function. The complexes can be formed between inhibitors and third molecules as well such as, co-structural molecules and reagent ions or surfactant molecules. In the case of the CMBT complex, it is formed by a salt linkage or ionic bond though the electrostatic attraction between the negatively charged MBT<sup>-</sup> and the positively charged cationic surfactant CTAB. Non-covalent bonds are weak by nature (typically several kcal mol<sup>-1</sup>) and allow a rapid response to environmental changes, such as a chemical or an energy change.<sup>26</sup> When an ionic compound, such as NaMBT, is entrapped, its solubility and mobility can be significantly reduced as a result of the complex formation. Analysis of an SEM image of the prepared CMBT cores with irregular morphology are shown in Figure 2a. It is confirmed that the average size of the CMBT initial particles is 4 μm. The initial cores can release the immobilized inhibitors when the temperature increases and the released NaMBT inhibitors form crystals when the temperature decreases. Figure 2d shows that the released inhibitor, NaMBT, starts to crystallize from the melted initial cores after heated. The initial solid core formed by surfactant-immobilized inhibitor, CMBT, can consecutively induce a sol-gel reaction in which silica forms porous inorganic shells around them. SEM observations show that the resultant SiNaMBT particles are around 5 μm in diameter with CMBT initial particles encapsulated inside (Figure 2b). Figure 2c shows that the inhibitor, NaMBT, is released from the melted initial cores of the porous silica carriers after heating.



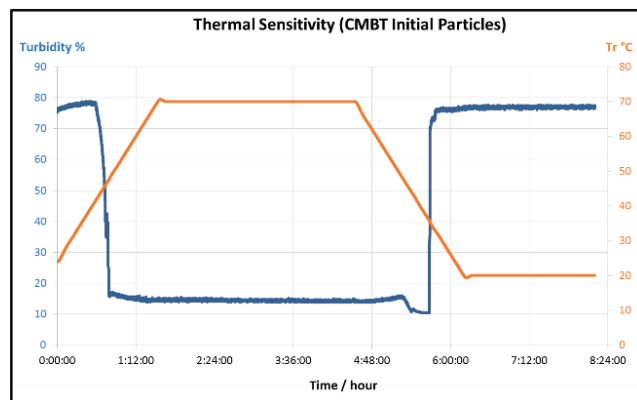
**Figure 2. SEM micrographs of (a) initial core CMBT, (b) silica encapsulated thermal and pH-sensitive particles SiNaMBT, (c) heated SiNaMBT, and (d) heated CMBT.**

The thermal stability of the resulting initial cores of CMBT and carrier particles SiNaMBT was investigated using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) (as shown in Figures 3a and 3b). The small weight loss of CMBT and SiNaMBT below 100°C can be attributed to the loss of adsorbed water. No weight loss related with water adsorption was observed for pure CTAB. There was also no water evaporation above 500°C for the SiNaMBT sample, proving that the condensation of silanol was completed.<sup>17</sup> The second decomposition temperature of 130°C for both the spray dried CMBT and SiNaMBT, which is lower than that of pure CTAB, can be attributed to the complete removal of the organic complex CMBT. The thermal stability of SiNaMBT, which is not higher than that of CMBT, implies that encapsulation in the inorganic porous silica shell didn't affect the thermal sensitivity of the initial core. The residual weight of the SiNaMBT carriers, after the primary and secondary weight loss, was approximately 40%, corresponding to an encapsulated initial core content of approximately 60%. However, for CMBT, the primary weight loss, corresponding to the release of NaMBT, was approximately 40%. These results indicate that the actual content of encapsulated NaMBT was in the 35-40% range, in good agreement with what was determined by elemental analysis. DSC experiments clearly demonstrated that the melting range of the SiNaMBT particles was slightly broader than for the core CMBT. The first melting peak of SiNaMBT is at a higher temperature than that of CMBT, which shows that the highly cross-linked shell slowed the heat transfer and prevented the leakage of the melted core. The two peaks of CMBT are exceptionally separated from each other, indicative of a melting-recrystallization-melting process during heating. It can be hypothesized that the two peaks are assigned to the melting of the CMBT component and the melting of NaMBT released, respectively.

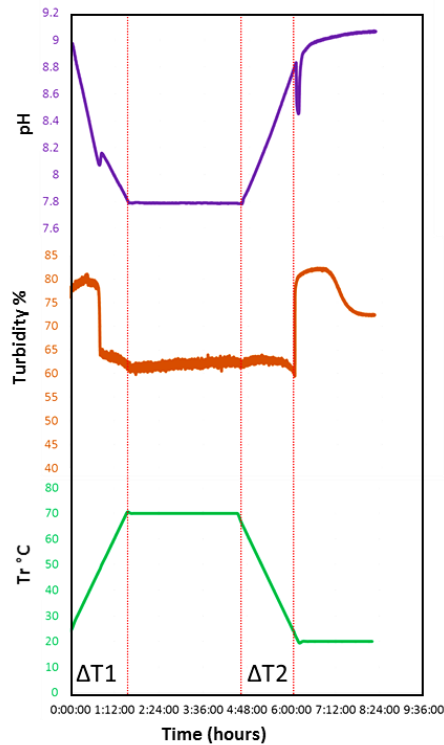


**Figure 3. (a) TGA weight loss curves for CTAB, NaMBT, CMBT, and SiNaMBT, (b) DSC curves for CMBT and SiNaMBT. All TGA tests were performed at a heat rate of 5 °C min<sup>-1</sup> in a nitrogen (N<sub>2</sub>) atmosphere.**

The controlled release behaviors of different particles were monitored by observing the change in the turbidity of the solution when the temperature or pH, which acted as stimuli, were varied. The *in situ* analysis of turbidity was done qualitatively to find out how much solid phase was present in the solution. As shown in Figure 4, the turbidity of the CMBT particles suspension dropped from 80% to 15% when the temperature of the colloidal solution increased from 25°C to 70°C. The turbidity went back up reversibly when the temperature was lowered to 20°C. It is worth noting that this change didn't show when the temperature was kept constant. A similar test was conducted on a SiNaMBT particles mixture (Figure 5.) with similar results.



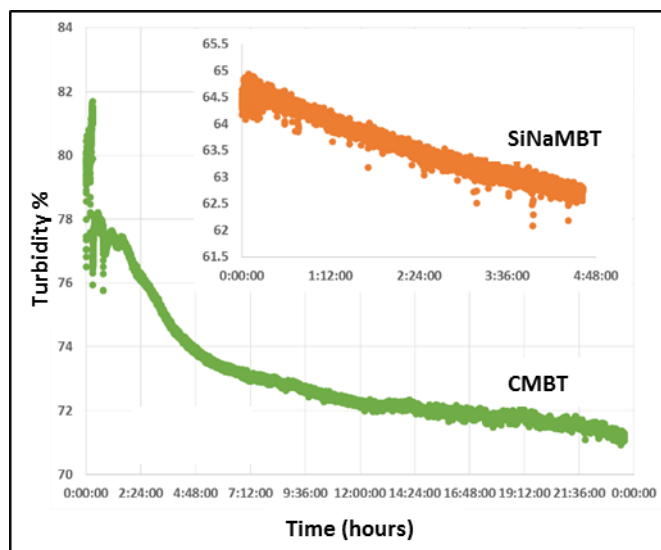
**Figure 4. Turbidity and temperature profiles versus time for CMBT particles**



**Figure 5. Turbidity, pH and temperature profiles versus time for SiNaMBT particles**

With increasing temperature ( $\Delta T1$ ) the turbidity of the colloidal solution of SiNaMBT decreased from 80% to 60%. Since the silica carrier was not sensitive to temperature, a higher turbidity at 70°C was observed. The pH was also recorded during the thermally reversible process. The pH of the solution dropped from 9 to 7.8 during the period when temperature was increased ( $\Delta T1 = 45^\circ\text{C}$ ), while it climbed back up to 9 when the temperature was decreased ( $\Delta T2 = 50^\circ\text{C}$ ). This demonstrated that this was a pH reversible process as well.

The pH sensitivity of CMBT cores and SiNaMBT particles was tested by adding hydrochloric acid (HCl) to the system while maintaining the temperature at 25°C. Figure 6 shows that the turbidity of both particle suspensions, CMBT and SiNaMBT, went down after the pH of the solution decreased to 2 and that the release was time dependent for both particles. This testing was done at room temperature, to eliminate the possibility of thermally-controlled release from these particles. The turbidity of both CMBT and SiNaMBT mixtures were still continuously going down after 12 hours and 5 hours, respectively, implying an immediate as well as prolonged release, processes under acidic conditions.



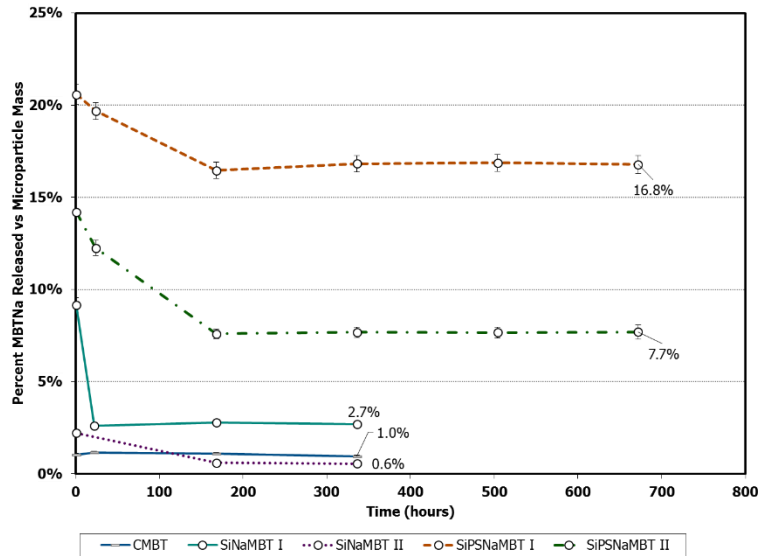
**Figure 6. Turbidity profiles versus time of the resulted SiNaMBT particles under pH = 2**

In order to increase the organic solvent compatibility of the inorganic carriers for better incorporation into epoxy based coatings, hybrid particles SiPSNaMBT were designed and investigated as well. These particles were dispersed into a KOH solution for a long period of time in order to study their release behavior under basic conditions. The pH-controlled release of NaMBT was monitored and the release profiles of NaMBT from particles are shown in Figure 7 where the percentage of NaMBT released was plotted as a function of time. Longer releasing time periods (in the range of a couple weeks) were obtained as compared to those obtained previously, which were of the order of a couple of hours. The release test data demonstrates an immediate as well as continued long-term release at pH 12. Interestingly, the data also indicates the recyclability of superfluous active substances. This is due to the increase in porosity that occurs when the inhibitor is released. On the other hand, the initial CMBT cores didn't show this recyclability which supports the conclusion that the recyclability may attributed to the positively charged porous framework of the carriers.

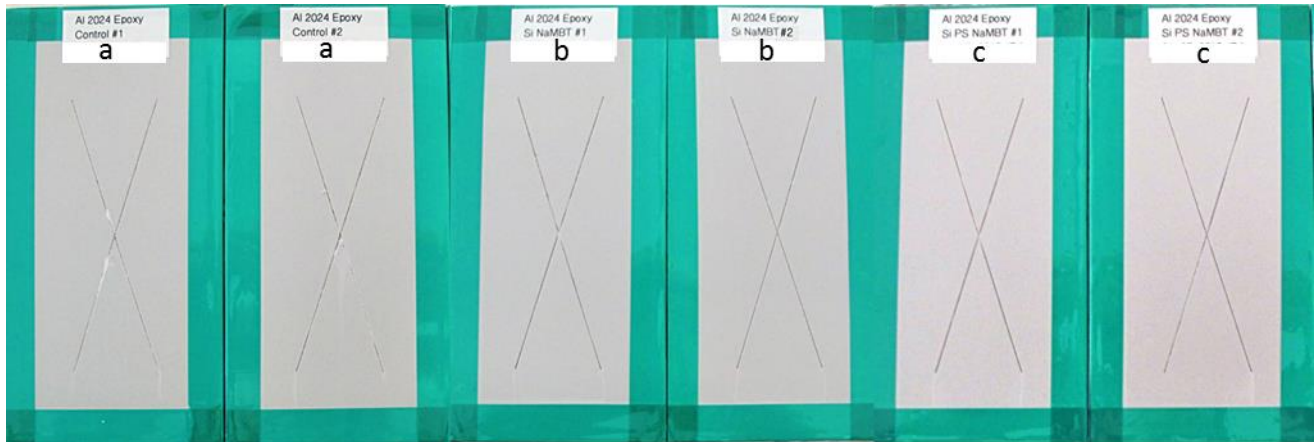
Two SiPSNaMBT particle formulas with different loading rates, labeled as SiPSNaMBT I and SiPSNaMBT II, showed that approximately 22 % and 14 % NaMBT respectively can be mobilized at pH 12 (Figure 7). Considering the total loading capacities of these particles, it must be kept in mind that partial inhibitor release may be caused by heating. Investigation of the thermal-controlled release properties of these particles is currently on-going in our lab. The release study in bulk solution demonstrated the instant and extended release and reuptake behavior of these carriers for superfluous inhibitive compounds. However, it is worth noting that the release behavior observed in the bulk solution is expected to be different from that in a coating at a corrosion site on a metal where the released active compound will be consumed.

The effect of the particles on the corrosion protective properties of various epoxy and waterborne coatings was evaluated on coated panels by observing the formation of corrosion products and blisters along the scribed area and overall surface on steel and aluminum substrates. The appearance of aluminum 2024-T3 panels coated with epoxy resin (control), epoxy resin with SiNaMBT, and with SiPSNaMBT, after exposure to salt fog for 500 hours, are shown in Figure 8. Test were conducted on duplicate panels to check the reproducibility of the results. Figure 8a (Control 1 and 2) show the appearance of corrosion





**Figure 7. Release profile of NaMBT from CMBT, SiNaMBT and SiPSNaMBT particles in KOH aqueous solution at pH 12 with different loading rate.**



**Figure 8. Digital pictures taken after 500 hours in the salt fog chamber of duplicate panels of aluminum 2024-T3: (a) epoxy coating (control), (b) epoxy coating with SiNaMBT, and (c) epoxy coating with SiPSNaMBT**

products and a few blisters along the scribes while very few corrosion products could be observed for the epoxy resin with SiNaMBT (Figure 8b: SiNaMBT #1 and #2). However, no apparent corrosion products were observed on the epoxy resin with SiPSNaMBT (Figure 8c: SiPSNaMBT #1 and #2). These results show that the incorporation of SiNaMBT or SiPSNaMBT can effectively improve the corrosion protective properties of the epoxy coating without affecting the adhesion properties.

## CONCLUSIONS

Two novel inorganic carriers for dual-stimuli controlled, on-demand release of corrosion inhibitors were synthesized and tested using a water soluble corrosion inhibitor. The ionic corrosion inhibitor, NaMBT, was encapsulated by a one-pot *in situ* reaction into a silica framework in order to achieve pH- and thermal-controlled release properties when incorporated into a corrosion protective coating. A complex core was formed by a reaction between surfactant molecules, CTAB, and the payload inhibitor, NaMBT. The complex not only immobilizes the water soluble ionic inhibitor for encapsulation into silica carriers but also provides the resultant particles with thermal and pH sensitivity to achieve multi-stimuli controlled release for corrosion protection purposes. The release test data demonstrated both immediate and prolonged response to pH values of 12 and 2. Interestingly, the data also indicated the recyclability of superfluous active substances.

This work is also involved the synthesis of controlled-release organic/inorganic hybrid carriers that can be effectively integrated into various coatings for autonomous corrosion protection. Accelerated corrosion tests showed that the corrosion protective properties of an experimental epoxy coating on aluminum 2024-T3 were improved when the two carriers were used to incorporate NaMBT into the coating.

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