Multi-functional low-cost epoxy based nanocomposite corrosion resistant coatings

Pranav Nawani, Natalie Gese

Applied Sciences Laboratory (ASL) Washington State University (WSU), Spokane, WA

Corresponding author: Pranav.nawanni@wsu.edu*, Phone: (509) 358-7845.*

Abstract:

"An ounce of prevention is worth a pound of cure." — *Benjamin Franklin*

Corrosion is a significant global issue, resulting in high maintenance and repair costs. Long term structural integrity of metal and its products is directly dependent on its anti-corrosive properties. Surfaces exposed to marine environments are prone to microbial attachment followed by biofilm formation, resulting in bio-fouling. Hence coatings are used to protect the surfaces against corrosion and biofilm formation. Currently various organic coatings are used to protect metals and the cost of these coatings is directly dependent upon the cost of the fillers used to impart specific properties. Conventionally fillers such as zinc, Titanium and Silver based compounds are used in coatings for corrosion and/or microbial protection of surfaces, which are expensive. The underlying issue with using these compounds as fillers is that they can adversely effect mechanical and barrier properties, due to which they are used as a base coat and additional fillers are used to compensate for such property losses. Most of these coatings need an enhanced anti-microbial surface and improvement in their barrier efficacy against water/moisture, oxygen, and chloride ions. Hence it is imperative to develop low-cost fillers that will enhance both active & passive corrosion resistance properties, prevent microbial attachment on the surfaces and will not degrade any polymeric properties. In this work, ASL is developing a *multi-functional* low cost epoxy-clay nanocomposite coating, for microbial and corrosion resistance. *Multi-functional* coatings are developed using a *multi-component* approach, where the innovation lays in deriving the benefits of various fillers through a combinatorial approach to synergistic harvesting of functionality and vigor. The primary filler is a naturally abundant clay material and, owing to their sheet like morphology and layered structures, their surface can be modified to achieve the desired property enhancements. Sheet like morphology enhances polymer filler interactions, resulting in enhanced mechanical and reduced barrier properties. The presence of clay in the coating materials will mitigate the impact of moisture and chloride ions (in marine environment) providing passive protection to the coated surface. Modification of clay with transition metal ions (TMI) enhances corrosion resistance properties of coatings.

Introduction:

Steel is an integral part of our life and is extensively used in automotive application, household appliances, equipment, defense, marine and infrastructure. Steel is highly susceptible to corrosion which may result in damages, down time of machinery, and accidents due to failure of equipment. Corrosion is one of the largest single expenses in the US economy and the total annual corrosion costs is approximated to be above \$1 trillion[1] and will continue to grow. Though researchers and industry have been working on developing various coating technologies to prevent corrosion, no common solution is yet known. Corrosion initiation reactions depend primarily on environment and substrate. Protection from corrosion can be very expensive, time consuming, and may also require high maintenance costs. A variety of successful corrosion inhibitors such as chromium and lead based materials have been banned due to their toxic & carcinogenic properties and environmental impact. After lead-based paints/fillers were banned zinc based coatings became more popular commercially and have proven to be very effective for corrosion resistance[2]. Zinc based coatings are expensive and when used as a filler it deteriorates the polymeric property of resin and hence is always used as a filler material in base coat. There is a continuous need to develop novel material for corrosion resistance coatings.

In marine environments, where materials are submerged in sea/ocean water, there is high risk of fouling due to the presence of microbes which attach themselves to the surface resulting in biofilm formation. This eventually leads to the growth of barnacles resulting in biofouling. Fouling causes decreased efficiency of ships & boats, and reduces the lifetime of various materials used for docks water sports equipment etc. exposed to marine environment. Fouling has high impact on the marine industry due to increased maintenance costs[3]. Hence coatings are required which will resist any biofilm formation and inhibit fouling in the marine environment.

Metallic and organic coatings are commonly used for the protection of the surface from corrosion and fouling. Effectiveness and usability of such coatings depends on various economic and environmental factors. Organic coats allow easy permeance of moisture, chloride ions etc. making the surface underneath susceptible to corrosion reaction. Inhibition of such reactions on the surface can be provided if the permeability of the coating material is reduced.

The architecture of polymer nanocomposites provides an excellent example of property enhancements as the studies have shown that polymeric nanocomposites have enhanced mechanical, excellent barrier resistance, flame retardancy, scratch/wear resistance, optical

characteristics and electrical properties[4,5]. Most of these property enhancements in polymer nanocomposites are accounted for by the filler-polymer interactions and aspect ratio of fillers. Similar architecture can be exploited in developing polymeric coatings. Similarly, in organic coats a variety of nanoparticles[6] are used to achieve property enhancements and providing passive protection to the surface. Researchers and industry are exploring various methods and materials for developing corrosion resistance materials and coatings. Commonly explored and used nanoparticles for developing organic coatings are titanium dioxide[7], zinc[8,9], clay[10,11], zeolites[12,13,14], ceria[15,16], ceramics[17], zirconia[18] and graphene[19] but most of these material have shown limited commercial success, either due to cost, toxicity, or availability. Some of these fillers may have adverse effect on polymeric properties of coatings especially mechanical and barrier properties. The barrier properties of the polymeric material can be improved by inclusion of appropriate fillers such as clay which has sheet like morphology[20,21,22].

Cost of coating material is directly dependent upon the cost of fillers used to impart specific properties and in this work, our focus is on developing low cost clay based fillers for application in corrosion resistance. These low-cost fillers when dispersed in epoxy or other organic resins will be used to protect surfaces especially metals against corrosion and fouling. We have developed fillers which have shown promising results in anti-corrosion and anti-bacterial properties. These are modified clay[23] based fillers and are easily dispersible in polymer matrices. Unlike zinc and other metallic fillers clay based fillers do not deteriorate polymeric property, on the contrary these are used as filler for enhancing various polymeric properties such as mechanical, permeability, etc. The clay has layered structure which provides large surface area for tailored modification to achieve various specific property enhancements. Exploiting the layered structures for clay modification can be carried out and these modified clay particles when dispersed into polymer matrices will provide impermeable silicate sheets and impart specific properties, dependent on modification. We have focused on the use of TMI's, especially copper for modifying clay and achieving corrosion resistance properties. Copper is also knows as common antibacterial and antifouling agent hence copper modified clay is expected to have multiple functionalities. Dispersion of TMI modified clay in the polymer matrix will provide multiple benefits at a very low cost and reduce or eliminate use of conventional fillers like zinc or titanium dioxide used as anti-corrosive and/or anti-microbial agents in paints and coating.

Principles of corrosion:

Commonly corrosion is defined as a electrochemical reaction, usually with metal and its environment where cathodic and anodic reactions occur simultaneously. The presence of metal, oxygen, water, chloride ions and/or microbes are required to initiate and sustain a corrosion reaction. The coating layer around steel provides a passive layer, which is electrically neutral and corrosion initiates with the destruction of this layer making free electrons available for the chemical reactions to occur. For a typical steel surface, the following reactions occur during corrosion:

Anodic reaction: It begins with the oxidation of iron atoms due to the destruction of passive layers, which in the presence of diffused oxygen forms rust:

Cathodic reaction: The free electrons generated at the anodic reaction site move through the steel and react with water to form hydroxide ions, which helps in sustaining the anodic reaction.

Figure 1 depicts a typical corrosion reaction, where metal or steel acts as an electrode. Schematics of electro flow and corrosion reactions are shown.
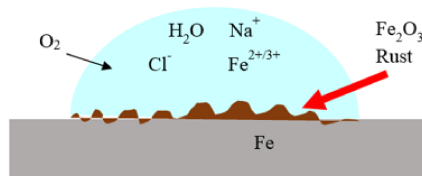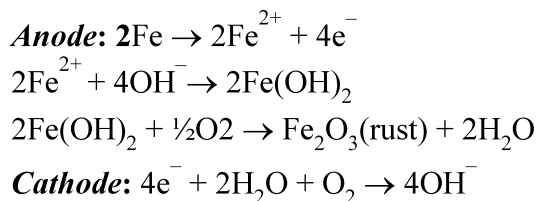
$$\textbf{\textit{Anode}: } 2Fe \rightarrow 2Fe^{2+} + 4e^-$$
$$2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2$$
$$2Fe(OH)_2 + \tfrac{1}{2}O2 \rightarrow Fe_2O_3(rust) + 2H_2O$$
$$\textbf{\textit{Cathode}: } 4e^- + 2H_2O + O_2 \rightarrow 4OH^-$$

Figure 1: A typical corrosion reaction occurring at the surface of steel substrate in salt water.

These anodic and cathodic reaction sites constitute to form a corrosion cell and many such cells may exist simultaneously on the same metal surface. To prevent the corrosion reaction, it is important to mitigate the diffusion of chloride ions and moisture (water and oxygen) into the surface. These reactions may proceed differently in different metals, but overall the corrosion reactions follow principles of electrochemistry.

In this study, we have investigated new epoxy based *multi-component* nanocomposite coatings using transition metal ion modified clay based fillers such that various properties of polymer matrix are enhanced and key corrosion resistant properties are addressed. The objectives are to

prevent corrosion by benefitting from individual properties of fillers and to address various property enhancements required for corrosion resistant coatings. A multi-pronged strategy to fight corrosion will be adapted to develop multi-component coatings that will provide the coated surface corrosion resistance: These coatings will be developed using non-toxic, low cost, modified fillers and co-fillers that will be well dispersed in an epoxy matrix. Modification of the clay surface will provide it with multi-functional characteristics that will help to develop coatings that inhibit the passage of moisture, oxygen, chloride ions, and provide impedance to the cathodic current.

Experimental:

Sample preparation:

i) Clay Modification: We have investigated the use of commercially available clays, montmorillonite or Cloisite®Na$^+$ (MMT) and organically modified montmorillonite, Cloisite®20A (C20A) for modification and dispersion. C20A is an organophilic bentonite derivative of montmorillonite obtained by modifying montmorillonite with an organic surfactant bis (hydrogenated tallow alkyl) dimethyl quaternary ammonium salt. These clays were suspended in a transition metal ion (TMI) solution for ion exchange. For modification of each 10 g of clay, 200 ml TMI solution was prepared. Details of the TMI solutions used for modification are summarized in Table 1. MMT and C20A clays were received as samples from BYK additives (formerly Southern Clay Products). ACS grade reagent salts, solvents, and reducing agent were procured from Alfa Aesar, Sigma-Aldrich, and J.T. Baker.

Reagent	Solvent	Concentration (M)
Cu (II) chloride	Methanol	0.3
Fe (III) chloride	Methanol	0.3

Table 1. Summary of various TMI salt solution used for C20A modification.

Solutions for ion exchange were prepared by dissolving TMI salts in methanol. The clay-TMI solutions were stirred in covered beakers for approximately 48 hours at ambient conditions. During this time surfactants and interlayer ions present in the clay exchanged with transition metal cations in the electrolyte solution. The concentration of the TMI in the electrolyte was added in excess of the required cation exchange equivalency (CEC) of 95 meq/100g for C20A [24,25]. Following the

modification process, the clay suspensions were filtered under vacuum, using Whatman no. 1 filter paper and washed with 20 ml of clean methanol per gram of C20A precursor material. Two iterations of filtering and washing has been shown to be sufficient for removing residual salt content [26,27]. After filtration, the modified clays were then dried in a vacuum oven at 40 ˚C for fifteen hours to remove residual solvent. The dried clay samples were then ground into fine powder using a mortar and pestle.

iii) *Dispersion of fillers in resin:* Hexion Inc. provided samples of EPON® resin 1001-CX-75 and EPIKURE® curing agent 3115-X-70, an amine cured epoxy system which was used for coating development. Nanocomposites were prepared by dispersing 3 wt% modified clay in the EPON resin and Epikure curing agent. To aid clay intercalation and exfoliation, modified clay was first dispersed in the resin component by shear mixing at a rate of 6,000 rpm for 5 minutes (IKA T25, Ultra TURRAX) followed by sonication (VWR B2500A-MT) for 10 minutes, repeating each step once. The curing agent was then added to the resin-clay mixture, 7 parts curing agent to 20 parts resin, and hand mixed followed by vortex mixing for 1 minute each. The resin was applied to SAE 1008/1010 grade carbon steel (ASTM 1008) test coupons (Q-panel, R 23.5, size 3.5 x 2 x 0.032 in).

iv) *Coating of samples:* The test coupons were coated with different thicknesses. For varying thicknesses, a 3/8-inch applicator brush or Spin Coat G3P-8 coating system was used. For brush application, the coatings were applied by weight and evenly distributed over the surface of test coupon with the applicator brush. Spun coating was applied in a two-step cycle, at 500 rpm for 30 seconds, and at 2000 rpm for 15 seconds.   Once coated samples were prepared, the coating was cured for 24 hours under ambient conditions and then post cured at 60 ˚C for 1 hour).

Structural characterization:
For morphology, microstructure, and elemental analysis of the modified clay samples, an FEI Nova Nano Scanning Electron Microscope (SEM) equipped with an Oxford INCA X-max SDD 80 mm^2 Energy Dispersive X-ray Spectrometry (EDS) detector were used. Clay powder samples were applied to carbon adhesive attached to aluminum substrate and sputter coated with 10 nm of gold for SEM and EDS analysis. FTIR analysis of the modified clay samples was carried out to

obtain information on composition and structure using an Agilent Varian 680 FT-IR spectrometer in ATR mode scanning in the 4000 – 400 cm-1 range. The IR spectra were obtained at 2 cm^{-1} resolution with 16 scans per sample.

Electrochemical measurements:

Linear polarization (Tafel) and EIS spectra were obtained using a CHI 760D potentiostat (CH Instruments Co., Ltd.) in a faraday cage using a three-electrode cell configuration (Gamry PTC$_1$). The coated test coupon (7 cm^2 exposed surface area), a 3-mm diameter carbon rod, and saturated calomel electrode were used as working, counter, and reference electrodes, respectively. All measurements were carried out 3.5 wt% NaCl electrolyte solution under ambient conditions.

Accelerated corrosion test:

Test coupons were subjected to accelerated corrosion testing in a controlled corrosion chamber by subjecting continuously to 3.5 wt% NaCl salt fog at 35 ˚C for 30 days in a salt fog corrosion cabinet (Auto Technology, 55-gal reservoir) operated in accordance with ASTM B117 test method[28].The nanocomposite coating systems were evaluated for corrosion resistance performance according to the ASTM D610, D714, and D1654[29, 30, 31]. Prior to commencing accelerated corrosion testing in the salt fog chamber the samples were scribed using a scribing tool and length of the scribe was approximately 1cm and for consistency all samples were scribed in one direction, then weighed.

Result and Discussion:

The coatings developed and investigated in this study are expected to have properties to ensure low-permeability, improved mechanical properties and improved resistance towards corrosion. In this study, we have investigated use of commercially available clay montmorillonite and its organic analog Closite 20A. Figure 2 a) shows schematics of clay particles and its layered structure. Figure 2 b) schematics of morphology of clay particles when dispersed in polymeric resin forming various orientation of layered and exfoliated clay particles. Upon mixing, orientation of clay particles can play a key role in defining the permeability properties. Extensive shear forces result in breaking up of larger clay particle into mixed morphological structure of small clay tactoids and individual layers which are randomly oriented in the matrix.
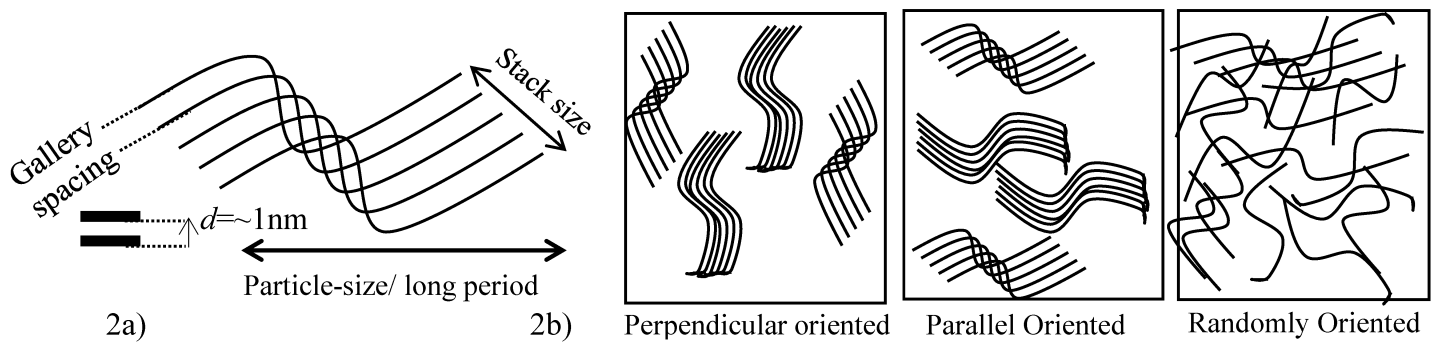
Figure 2a): Layered structure of clay; b) morphology of clay when dispersed in polymer matrix.

Due to slow relaxation time and flow of material in coatings, smaller clay tactoids tend to align parallel to the surface, hence providing maximum improvement in permeability properties. The clay galleries are ~ 1 nm in inorganic clays and can be up to 3 nm in organically modified clays. These galleries available for modification with organic ions and/or inorganic metals.

Commercially available clays were modified using various transition metal ion salts and their representative samples are shown in Figure 3.
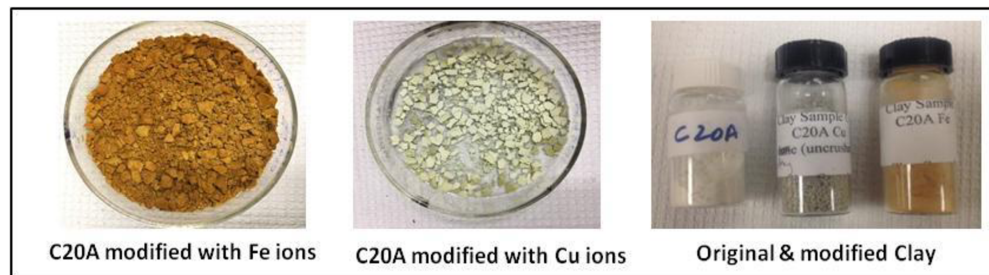

Figure 3: C20A clay modified using various transition ion salts (FeCl$_3$ and CuCl$_2$)

Processing parameters of modifications were altered to achieve variation in TMI content of modified clays. Unmodified and modified clays samples were dispersed in epoxy matrix and nanocomposites samples were prepared. Processing conditions for dispersion were kept identical for all samples for consistency. Clean as received carbon steel panels were coated with epoxy nanocomposites coatings in various thicknesses and using various methods.

Dispersion of MMT and MMT modified using various transition metal ion salts was attempted, however, the MMT clays were observed to settle due to their hydrophilic nature and would not completely disperse in the hydrophobic epoxy, therefore, the MMT based clays were not further investigated for this study. MMT modified clays are presumed to have better dispersion in water based epoxy due to the hydrophilic nature of the MMT clay and these modified clays are expected

to show property enhancements in water based epoxy resins. Further investigation proceeded using C20A and modified C20A clays.

Structural analysis using FTIR: Below, Figure 4 shows a representative FTIR spectra for unmodified and modified clays. Figure 4a) shows strong absorbance between 2950 and 2850cm⁻¹, which is due to CH stretching in the surfactants present in C20A. In the Figure 4b) reduction of absorbance peaks in FTIR data at 2950-2850cm⁻¹, suggests removal of surfactants took place upon transition metal ion modification. Further complementary data was obtained using EDS and SEM, which is in agreement to FTIR findings as well. Detailed FTIR data as shown in Figure 4 indicates that modification of clay has taken place. Unmodified clay shows OH stretching at 3630cm⁻¹, and this peak reduces in modified clays.

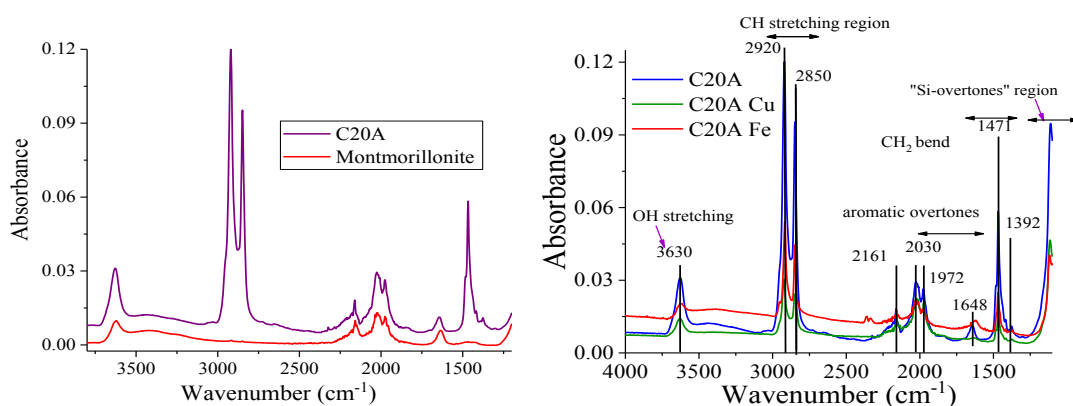*Figure 4: a) FTIR data of C20A vs montmorillonite clay, b) Cu and Fe modified C20A clays*

The doublet appearing at 2920-2850cm⁻¹ are representative C-H stretching peaks. In the modified clays the reduced intensity of CH stretching peaks suggests that the concentration of surfactant has reduced, which is expected if modification has taken place. Absorbance peaks at 1471 and 1392cm⁻¹ are for CH₂ bending vibration from surfactants. As the surfactant reduces upon modification the intensity of these peaks reduces. Peaks in the region 1600 to 2000cm⁻¹ are aromatic overtones while peaks appearing below wavenumbers 1000cm⁻¹ are Si overtones coming from structure of clay.

Composition and morphology of clays using EDS and SEM: Modified clays were characterized for their morphology using SEM micrographs and TMI content using EDS. In the Figure 5, shown below are the SEM images of unmodified and TMI-modified C20A clays. The clay surface does not show

any agglomerates of metal crystallites suggesting that the TMI intercalates the gallery spacing of clays. Further investigation of the clay structure will be achieved using X-ray spectroscopy to confirm this.
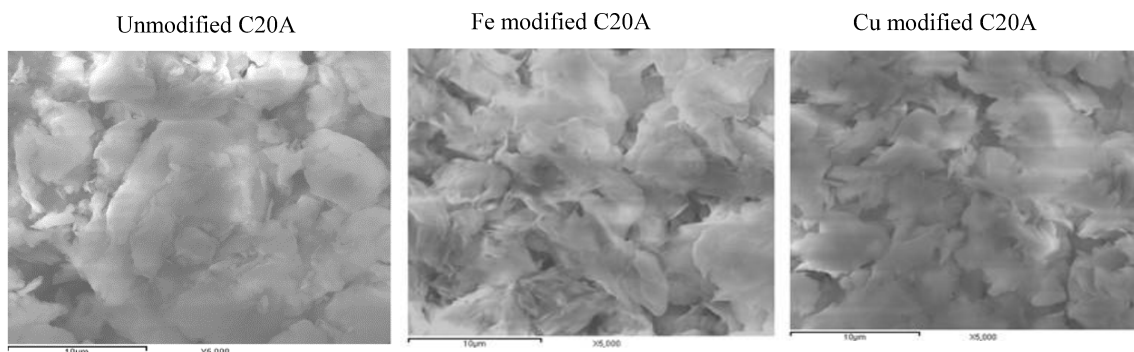
Unmodified C20A   Fe modified C20A   Cu modified C20A

Figure 5: SEM secondary electron images of Fe, and Cu modified C20A, 5kX magnification

EDS spectra was obtained of the clay samples to estimate the elemental compositions. EDS results showing the presence of TMI ion in the clays and main elements of the clay are tabulated in the Table 2. The EDS data is evidence that the clay has been modified with TMI's and that the metal ions have successfully intercalated into the clay galleries. Further investigation using atomic absorption studies will be carried to determine precise % of transition metal ions in the modified clays.

Clay Sample	Na	Fe	Cu	C	O	Mg	Al	Si	Ca
Montmorillonite	1.89	2.35	-	-	55.25	1.6	9.85	28.13	0.58
Cloisite 20A (C20A)	-	2.28	-	30.11	37.53	0.88	7.94	20.48	0.19
C20A CuCl$_2$	-	1.83	3.33	24.86	41.76	0.83	7.14	18.04	-
C20A FeCl$_3$	-	4.92	-	31.76	40.83	0.73	6.70	16.48	0.14

Table 2: EDS composition analysis summary of the clays used for epoxy preparation.

Electrochemical Spectroscopy: Using unmodified and TMI modified clay nanocomposites were prepared and carbon steel coupons were coated and investigated for corrosion resistance properties using electrochemical spectroscopy. To evaluate the characteristics of various coating formulations towards corrosion resistance, electrochemical analysis was conducted in 3.5% NaCl solution as an electrolyte (as it is equivalent to % NaCl found in sea water). Representative Bode and Tafel plots obtained are shown in Figure 6 for various coating formulations and it was established that the rates of corrosion reaction is

reduced in presence of TMI modified clays. Bode plots show impedance in current and Tafel plots were used to calculate the corrosion rate.
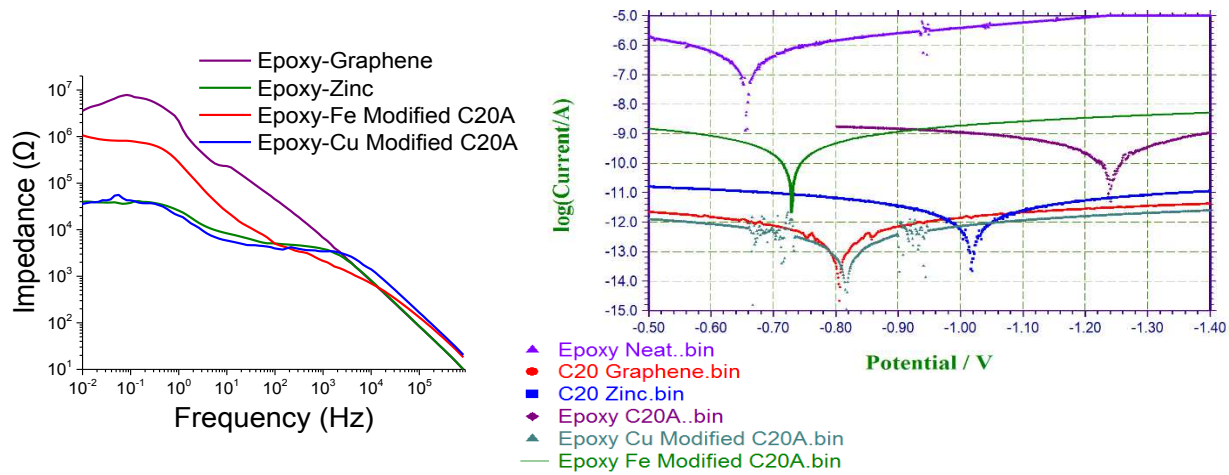

Figure 6: Bode and TAFEL plots of various representative coating formulations developed.

Effect of film thickness, loading and various modification of clay: Coating samples were prepared using various formulations of clays before and after TMI modification. Techniques of coatings, thickness of coatings, weight percentage of clay was varied to estimate effect of clay particles on the corrosion resistance properties. Corrosion rate (CR) is calculated using *Stern Geary* equation as per ASTM G102-89, **Corrosion Rate CR** $= (i_{corr} \times K \times EW)/\rho$, where i_{corr} is estimated from Tafel polarization curve, K = 3.27 x 10−3 mm g/μA cm yr, EW - Equivalent weight = 27.92 for steel and ρ = 7.87g/cm3 for steel.
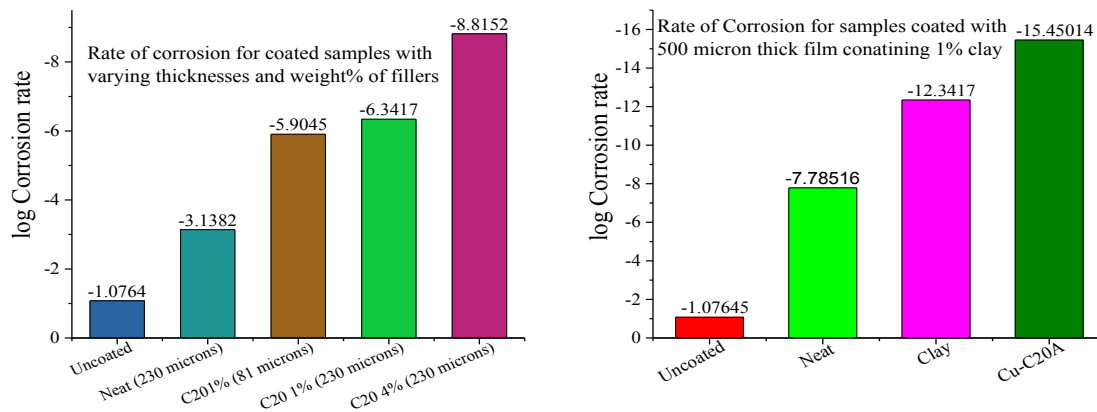

Figure 7a): Corrosion rate for varying clay contents and thickness of nanocomposite coatings.

b): Corrosion rate calculated for various modified clay used.

Coated samples with varying thickness of films and increasing the weight percent of fillers show reduced corrosion rates, as shown in Figure 7. This is expected as these two factors will reduce the permeability of moisture and chloride ions and the passive protection against corrosion is enhanced. Introducing TMI modification in the clay galleries further reduces the rate of corrosion, as the TMI in the clay galleries can provide the impedance to the corrosion current, hence we observed reduced rates of corrosion in coated samples containing TMI modified clays.

Synergy with co-fillers: To validate the corrosion resistance properties of these fillers a comparison against common corrosion resistance fillers is imperative. In this study, we have investigated a conventionally used corrosion resistant filler, zinc, to prepare various coating formulations. We have investigated it's behavior towards corrosion resistance and effect on corrosion resistance properties when used as a co-filler.

Samples were loaded with 3% modified clay zinc as a filler. Sample containing zinc as a co-filler had only 1% of zinc and 2% modified clay. Coupons were spun coated and approximate thickness of films was ~50 microns. Three coupons of each sample were evaluated for this experiment.
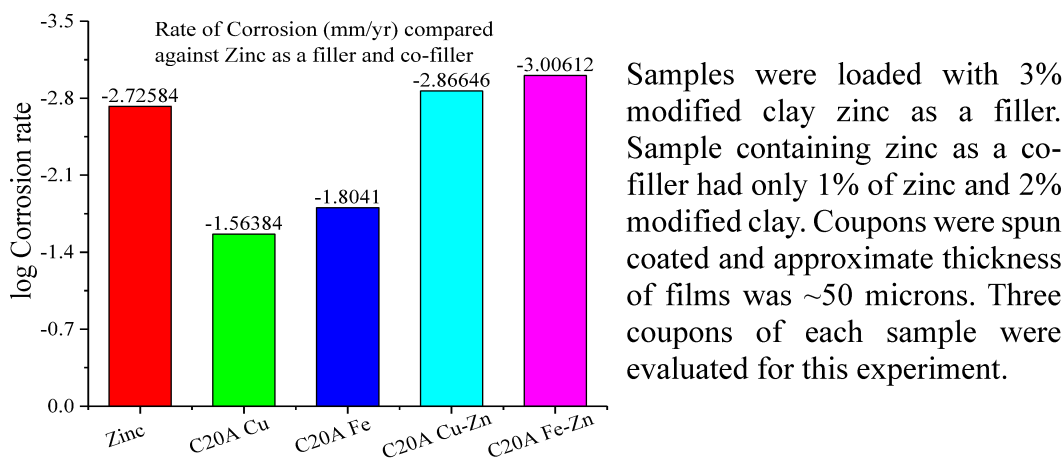
Figure 8: Validation of corrosion resistance behavior against zinc and Graphene as co-fillers.

Based on electrochemical data as shown in Figure 8 above, the corrosion resistance provided by zinc as a filler is higher than the modified transition ion modified. When zinc is used as a co-filler at 1 weight % the corrosion resistance of system is enhanced almost by 95%, which is evidence of a synergistic behavior when these fillers are used together. Further investigations are being done to improve and optimize these properties.

Accelerated corrosion test: Some of the preliminary results of carbon steel coupons coated with epoxy based nanocomposite coatings (only representative coupons are shown in Figure 9) and

scribed as per ASTM D-1654 are presented below in Figure 9. These samples were coated with epoxy based coatings containing unmodified and modified clay as labelled. The coated sample showed minimal rust formation after exposure for approximately 750 hours in accelerated fog chamber as per ASTM B117. In uncoated sample corrosion was very evident. All the coated samples were rated for rust grade as per ASTM D 610.
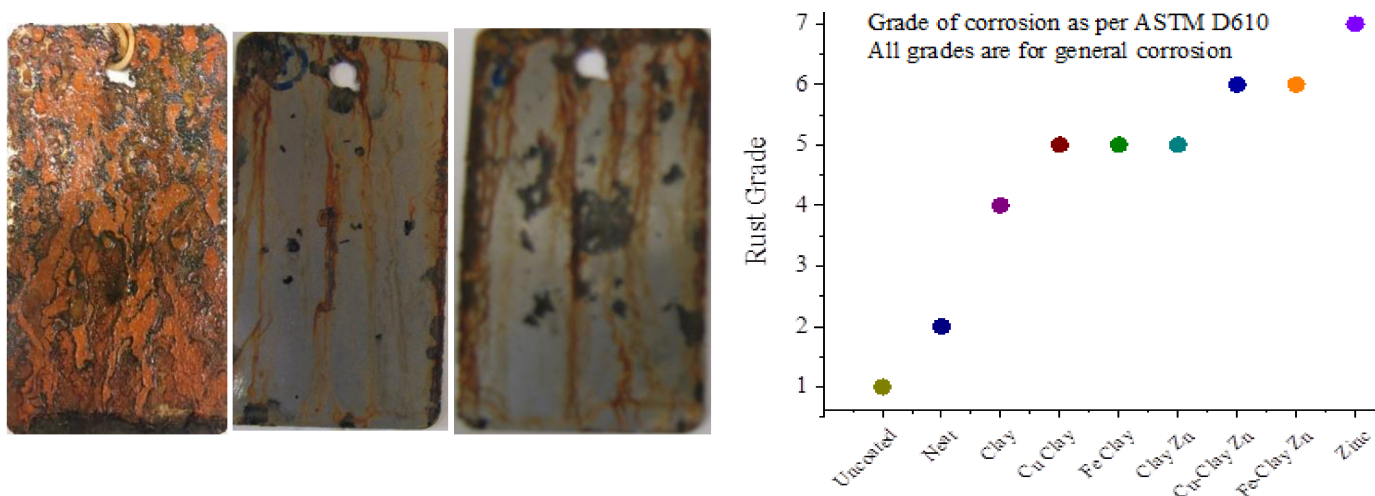

Figure 9: Rust grade estimated (as per ASTM 610) after the various coated panels (representative shown) were exposed to salt fog (as per ASTM B117) for accelerated testing.

Introducing clay in coating formulation qualitatively shows improvement in rust grade which is further improved when TMI modified clays were used. Using zinc as a co-filler along with TMI modified clay shows improvement in the rust grade.

Conclusion:

Coating samples using transition metal ion modified clays were prepared and demonstrated enhancement in corrosion resistance properties. Dispersion of uniquely modified clay based fillers in the epoxy matrix resulted in a superior coating, with enhanced anti-corrosive, properties. Due to morphology of the nanostructures formed and modification of clay in coatings dual active passive protection against corrosion takes place. The sheet like clay particles randomly orient in the coating matrix and reduces the permeability of moisture and chloride ions, thereby reducing the rate of corrosion. Modification of clay with transition metal ions in the presence of methanol, primary amines and unsaturated surfactants can result in mixed ionic state of TMI in gallery of

clay. The extremely charged inner layers of clay provide impedance in current which reduces the rate of corrosion. Through a *multi-component* approach that includes transition metal ion modified clays as primary fillers the investigation is driven toward development and usage of low cost and environmentally friendly materials. Low-cost clay based fillers can be used in paints and coatings for enhancing barrier efficacy, corrosion and mechanical properties to significantly improve protection of the coated surface and replace conventional expensive zinc fillers either partially or completely. Although, qualitative zinc based coating samples seems to be highest in rust grade but improvement in rust grade in presence of TMI modified clay is also of great importance. Electrochemical data suggests that when zinc is used as a co-filler due to synergistic behavior corrosion protection is significantly enhanced and surpasses when zinc was used alone as a filler. Clay also is known to show enhancements in mechanical property, reduced permeability. Further optimization of the investigated nanocomposite formulations could result in a unique nanocomposite coating, which could completely replace zinc as filler in the paint and coating industry.

Acknowledgement:

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