Evaluation of Nanostructured Polymeric Coatings for Steel Corrosion Protection

A. Aglan*, A. Ludwick** and M. Reeves**

*Chemical Engineering Department, Michigan Technological University, Houghton, Michigan, USA, aaaglan@mtu.edu

** Chemistry Department, Tuskegee University, Tuskegee, Alabama, USA, aludwick@tuskegee.edu

ABSTRACT

The effect of the addition of multi-walled carbon nanotubes (MWCNT) to epoxy and vinyl chloride/vinyl acetate copolymer (VYHH) coatings on their ability to protect the substrates was studied. Coatings were formulated from these resins with and without MWCNT reinforcement. Steel substrates were prepared and coated with each formulated coating and submerged in 5% NaCl solution to study effectiveness by means of Electrochemical Impedance Spectroscopy (EIS). Optical microscopy was used to capture the progress of sample corrosion. EIS measurements showed that the addition of MWCNTs to epoxy and VYHH coatings increased their charge transfer resistance in comparison with the neat coatings. This is an indication of the enhanced corrosion protection of the nanocoatings.

Keywords: vinyl chloride/vinyl acetate, corrosion, multi wall carbon nanotubes (MWCNT), electrostatic impedance

1 INTRODUCTION

Two main mechanisms are responsible for the breakdown of coating protection; diffusion of water through the coating and disbond propagation between the coating and the substrate. One technique that has recently been used to increase the adhesive and anticorrosive properties of polymers is the addition of nanoparticles [1]. Nanoparticles in the form of silicates, single wall carbon nano tubes (SWCNT) and multi wall carbon nano tubes (MWCNT) have been the most popular nano phases either as reinforcements or for specific functionalization [2-5]

Yang et al. studied the effect of pigment to binder ratio on the corrosion resistance of polyurethane coatings applied to carbon steel substrates [6]. The pigment to binder ratio affects the corrosion resistance. When they used nano zinc oxide, the optimum pigment to binder ratio was 0.3. The same ratio when they used conventional zinc oxide was 1.0. They concluded that nano zinc oxide particles have improved the anti corrosion resistance of polyurethane, resulting from the enhancement of the density of the coatings; this lead to the reduction in the transport paths, which blocked the penetration of the corrosive electrolyte to the steel substrates. The EIS measurements showed that there is an increase of three fold in the charge transfer resistance of the nano coatings compared with the conventional zinc oxide coating. The three-fold increase experienced with the addition of the nano coatings was observed through the 1000 hours of testing.

Chen et al. studied the effect of a nickel coating with carbon nano tubes on the corrosion resistance of carbon steel [7]. The coating was applied by electrochemical deposition. It was found that in 3.5% wt. NaCl solution the nano tube coating performed superior to pure nickel coating. The explanation for this was due to the fact that the nano tubes acted as a physical barrier more completely filling in the micro holes and flaws on the surface of the nickel coating. This explanation is similar to that given by Yang et al.

Characterization of various coatings using EIS requires an equivalent circuit, which consists of a combination of resistance (R) and capacitance (C) in various arrangements [8]. When a coated steel substrate is submerged in an electrolyte solution the first resistance R_1 represents the electrolyte resistance. The capacitance (C) represents the coating/electrolyte interface in the cell. The resistance R_{ct} in the Randle circuit is the polarization resistance or the resistance of the surface of the steel substrate to corrosion. The summation of R_1 and R_{ct} on a Nyquest plot represents the Charge Transfer Resistance, which can be used as a parameter to characterize the resistance of coatings to corrosion. Bard and Faulkner indicate that the real current voltage relationship in the electrochemical theory is nonlinear [9]. Loveday et al. state that as long as 10mV or less is used to measure the EIS current the current-voltage curve can be assumed to be linear. However, in some coating applications larger amplitudes can be applied [8].

In the present work, the effect of the addition of MWCNTs to VYHH (previously formulated [10]) and epoxy (commercial) coatings on their corrosion resistance is studied using EIS.

2 MATERIALS AND EXPERIMENTAL

The polymer resins used were an epoxy; *Valspar* Dura Build TM High Build Epoxy Finish comprised of resin A and hardener B in a 2:1 volumetric ratio. Resin A is a alkyd glycidyl ether and hardener B is isophorone diamine. Union Carbide's VYHH, which is a vinyl chloride/vinyl acetate copolymer, was also used. Multiwalled carbon nanotubes supplied by Ahwahnee Technology (Dia: 2-15 nm, Length: 1-10 µm , Layers: 5-20) were used as reinforcement in some systems. The VYHH and epoxy coatings were formulated with and without nanoreinforcements via sonication and asymmetric mixing techniques to achieve uniform dispersion. The coatings were applied to steel substrates (25mm X 101.6mm X 1.25mm). The steel substrates were prepared for coating by polishing and rinsing with acetone. Dried substrates were then dipped in the coatings with care taken to ensure an even coat with few defects. After 3 days of hang drying, samples were submerged in a 5% NaCl solution.

EIS measurements were conducted on unimmersed coated substrates through the use of the corrosion cell (or flat cell), shown in Figure 1. The flat cell was connected to a potentiostat (PARSTAT® 2273), supplied by Princeton Applied Research. The frequency range used in this experiment ranged from $1x10^6$ Hz to $1x10^{-2}$ Hz while the amplitude used was 10mV.

Optical microscopic observations, on the tested samples were performed. Measurements were taken of the $1cm^2$ portion of the sample that was exposed to the NaCl solution in the flat cell.

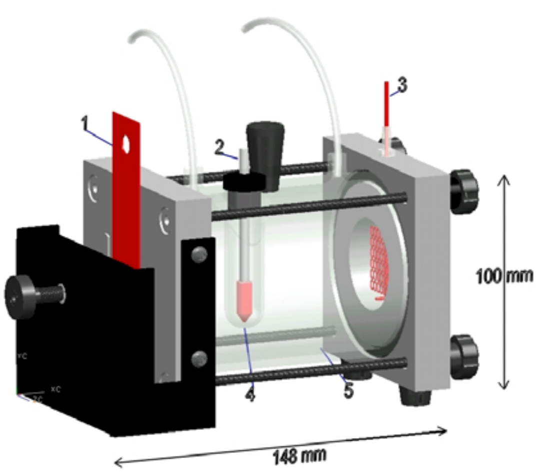

Figure 1. Flat Cell for EIS Measurements. (1) Working Electrode (Sample), (2) Reference Electrode, (3) Counter Electrode, (4) Reference Well, (5) Glass Chamber.

3 RESULTS AND DISCUSSION

3.1 EIS Measurements

In order to calibrate the set up which includes the PARSTAT® 2273 and the flat cell, the bare metal was inserted in the flat cell before and after 20 days immersion in 5% NaCl. The EIS measurement was carried out before immersion and a Bode plot was generated; after 20 days it was retested and a second Bode plot was produced. Figure 2 shows the comparison between no immersion and 20 days of immersion. The result of the charge transfer resistance (Rct) can be found by subtracting the minimum impedance from the maximum impedance. The value of Rct for no immersion was found to be 1250 **Ω,** compared to 550 Ω for that of 20 days immersion. As illustrated in Figure 2 the EIS measurement of the bare steel after 20 days immersion in 5% NaCl showed a decrease of more than 50% in the charge transfer resistance.

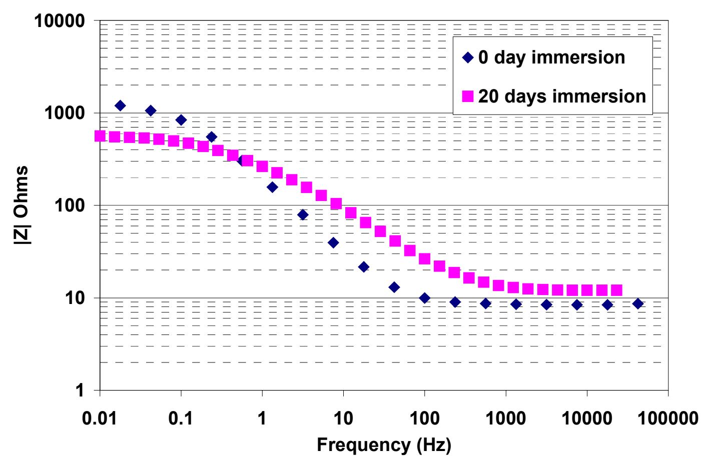

Figure 2. Bode plot of both 0 day and 20 days immersion of bare steel.

Results of EIS measurements are shown in the form of Bode plots in Figure 3 for both the neat and the nanoreinforced epoxy coatings. It can be seen that the nano epoxy coated sample displays higher impedance over the entire range of frequencies tested. The Rct from Figure 3 is about 2.08E9 for the nano-coated sample while that for the neat epoxy coating is only about 0.679E9. This indicates that the nano epoxy coating offers better corrosion protection.

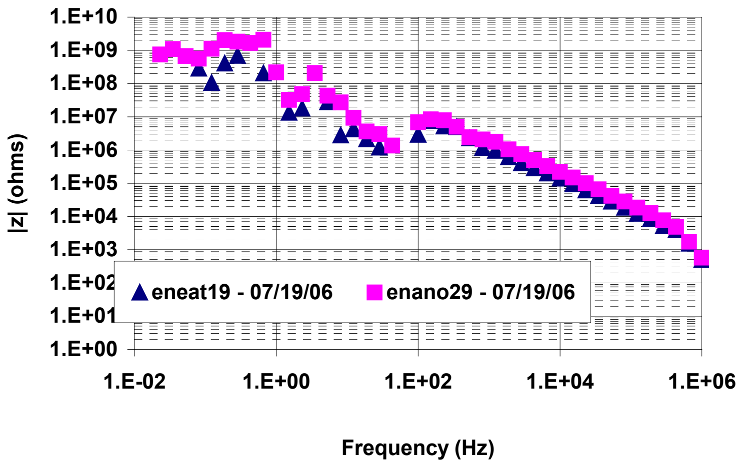

Figure 3. Bode plot of both neat and nano epoxy samples.

EIS measurements of the VYHH coated samples with and without MWCNT produced similar results, as seen in Figure 4. Again the impedance was greater for the nano specimen over the entire range of frequencies tested. The Rct from Figure 4 is about 1.38E9 for the nano coated sample while that for the neat VYHH coating is only about 0.345E9.

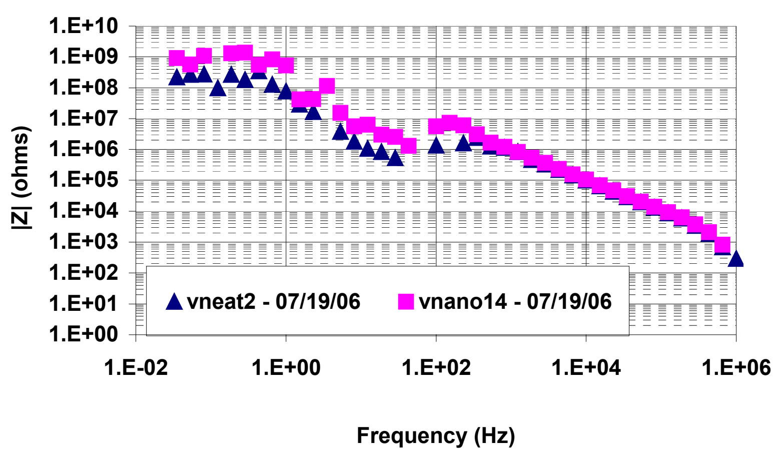

Figure 4. Bode plot of both neat and nano VYHH samples.

3.2 Immersion Test Observations

Visual and optical microscopy of the samples after 20 days of immersion in 5% NaCl solution was performed. For the bare steel it can be seen from Figure 5 that the surface has been adversely damaged; this was because no form of coating was added to aid in the prevention of corrosion.

.

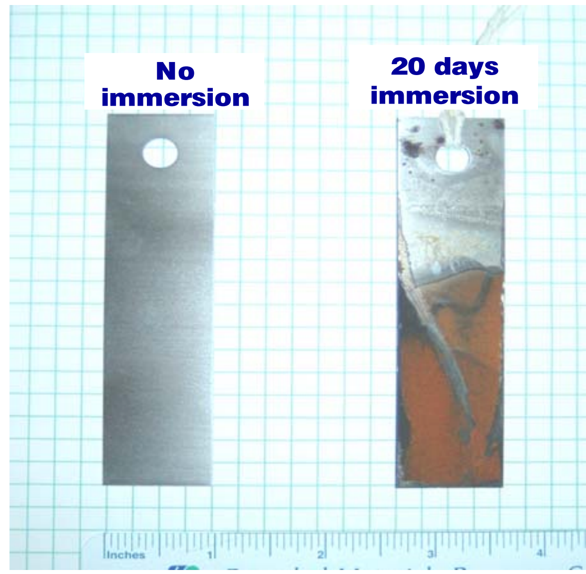

Figure 5. Corrosion characteristics of bare steel.

After 20 days of immersion the corrosion started on the edges of the neat epoxy coated samples, but the nano epoxy sample remained almost undamaged. This can be seen in Figure 6. Microscopic observation of the edge of samples with (right in Figure 6) and without MWCNT (left in Figure 6) after 20 days of immersion in 5% NaCl solution show the increased protection that the MWCNT has provided in the epoxy coating.

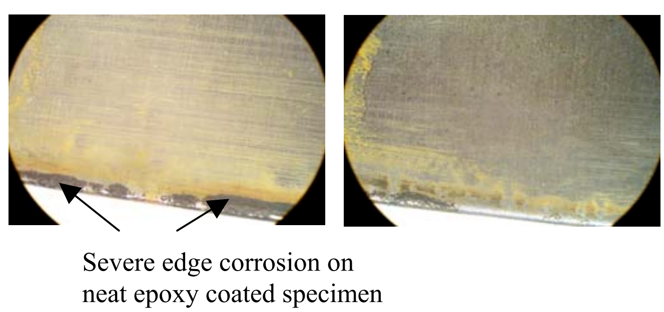

Figure 6. Optical micrographs of the neat and nano epoxy samples after 20 days of exposure to 5% NaCl solution.

Optical micrographs of the neat and nano VYHH samples after 20 days of exposure to 5% NaCl solution are shown in Figure 7. Blisters are seen in the neat coating on the left compared to the completely unmarred nano-coating on the right.

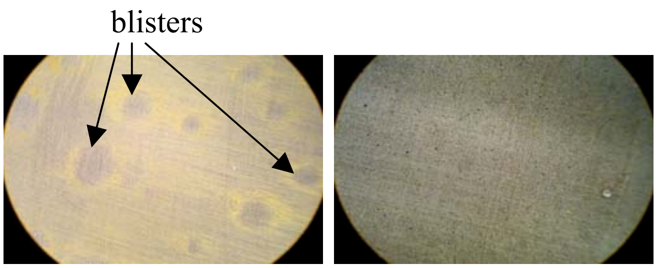

Figure 7. Optical micrographs of the neat and nano VYHH samples after 20 days of exposure to 5% NaCl solution.

Thus, the addition of a very small percent of MWCNT to the epoxy and the VYHH resins has improved the protection power of coating formulated from these systems. This finding has been verified from both the EIS measurements and the microscopic observations

4 CONCLUSIONS

Coatings have been successfully formulated containing MWCNT. EIS measurements have shown that the charge transfer resistance is higher for the nano coatings than the neat coatings for the epoxy and VYHH systems. Visual and microscopic observations have shown, based on 20 days 5% NaCl immersion, that nano reinforced epoxy and VYHH resins are better with respect to blistering and discoloration.

ACKNOWLEDGEMENTS

The NSF-REU at Tuskegee University supported this work. Dr. L Koons is gratefully acknowledged for his technical help. A. Allie, L. Allie, Maria Calhoun and Adam Charlton are gratefully acknowledged for their assistance.

REFERENCES

[1] http://www.inframat.com/hydro2.htm

[2] Hedia, H., Allie, L., Ganguli, S. and Aglan, H., The influence of nanoadhesives on the tensile properties and Mode-I fracture toughness of bonded joints. *Eng. Fracure Mech.* 73 (2006) 1826-1832.

[3] Ganguli, S., Aglan. H., and Dennig, P., Effect of loading and surface modification of MWCNT on the fracture behavior of epoxy nanocomposites. *J. Reinforced Plastics*, 25 (2006) 175-188.

[4] Ganguli,S., Bhuyan, M., Allie, L. and Aglan, H., Effect of multi-walled carbon nanotube reinforcement on the fracture behavior of a tetrafunctional epoxy. *J. Matrl. Sci. Letters,* 40(13) (2005) 3593-3595.

[5] Ganguli, S., Aglan, H. and Dean, D. Microstructural origin of strength and toughness of epoxy nanocomposites. *J. Elastomers and Plastics*, 37 (2005) 19-35.

[6] Yang, L.H., Liu, F.C., Han, E.H., Effects of P/B on the properties of anticorrosive coatings with different particle size. *Progress in Organic Coatings,* 53 (2005) 91-98.

[7] Chen, X.H., Chen, C.S., Xiao, H.N., Cheng, F.Q., Zhang, G., Yi, G.J., Corrosion behavior of carbon nanotubes–Ni composite coating. *Surface & Coatings Technology,* 191 (2005) 351–356.

[8] Loveday, D., Peterson, P., Rodgers, B., Evaluation of organic coatings with electrochemical impedance spectroscopy. *JCT Coatings Tech.*, (August 2004) 46-52.

[9] Bard, A.J., Faulkner, L.R., Electrochemical Methods; Fundamentals and Applications, Wiley Interscience, 2000.

[10] Mansour, E.M., A.-Gaber, B. Nabey, Tadros, A., Aglan, H., Ludwick, A., Solvent effect on the protection efficiency of vinyl resin varnish for preventing the corrosion of steel using electrochemical impedance spectroscopy. *Corrosion,* 58 (2002) 113-118.