Evaluation of Nanosilicate Filled Poly (vinyl chloride-co-vinyl acetate) and Epoxy Coatings

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ABSTARCT

The corrosion protection of nanosilicate filled poly (vinyl chloride - co - vinyl acetate) (VYHH) and epoxy resins has been studied. Nanosilicate was incorporated into VYHH at 0%, 0.5% and 1.5%wt loadings, and into epoxy at 0% and 1.5% loadings. Steel substrates were prepared and coated and films were casted with each of the prepared coatings for corrosion tests and mechanical tests, respectively. Some of the samples were submerged in 5% NaCl solution and tested periodically using Electrochemical Impedance Spectroscopy (EIS) and tensile testing. EIS measurements showed that VYHH/0.5%nanosilicate provided superior protection against corrosion. The nanosilicate filled epoxy exhibited increased resistance to corrosion after 21 days. The tearing energy of the neat VYHH coating decrease by 27% after 21 days of submersion, while the nano coatings showed a slight increase. The neat epoxy showed no change in the tearing energy after submersion, while that of the nano coating was increased by 14% after submersion.

Keywords: *Nanostructured, EIS Measurements, Tearing Energy, Differential Scanning Calorimetry.*

1. INTRODUCTION

Nano-polymeric coatings present a cost efficient and more durable protection against corrosion compared to conventional polymeric coatings. Research into these nano-polymeric coatings is directed towards exploring the superior properties that they exhibit, and also their applications as a solution to the costs in damage control and maintenance that the US is faced with each year due to corrosion.

Some conventional polymeric coatings for metal surfaces include latex paints, epoxies and polyurethanes. Over the years polymeric coatings are developed due to their good barrier properties. However, these pristine polymeric coatings are permeable to corroding agents such as water and oxygen [1]. In order to enhance the barrier properties of polymeric coatings some researchers have used various kinds of additives such as extenders and inorganic pigments which inhibits corrosion. Polymeric coatings can also be enhanced by using a conducting polymer either as a primer, blended with a conventional polymer, or as a coating itself [2]. One such example is the use of polyaniline incorporated in thermoplastic polymers such as poly (vinyl chloride-co-vinyl acetate) (VYHH) [3]. Significant improvement was observed in the corrosion protection of the coating when small amounts (0.2-0.3% w/w) of conductive polymer were added.

Another novel way to improve the properties of coatings is to add a nanophase to the polymer coating or the use of fillers in the form of nanoparticles in the coating. It can enhance the coating's effectiveness by filling the micro voids and crevices in the pristine polymer coating. The nanolayers formed also increase the diffusion paths of the corroding agent through the coating making it more difficult for the corroding agent to seep through [4]. Two fairly new and effective nanoparticles commonly used are carbon nanotubes (CNTs) and nanoclays. The use of CNTs as fillers for polymers and polymeric coatings has been explored [5, 6]. However, nanoclays still need attention as it has great potential to improve the barrier properties of the coating. Hang et al studied montmorillonite clay as a filler for epoxy coating [7]. There was significant improvement in the barrier properties of the coating compared to the neat coating with only 2% nanoclay. Another coating that is applicable in the shipping industry and is currently being studied is VYHH. VYHH formulated with methyl isobutyl ketone (MIBK) and toluene exhibits increased barrier properties as a coating compared to VYHH formulated with MIBK and Xylene or Benzene [8]. Aglan et al found that VYHH formulated with MIBK and Toluene, when reinforced with MWCNTs exhibited increased mechanical and corrosion protection properties when compared to neat formulations [6].

The evaluation of coatings is normally done by various methods. Some of the methods include Electrochemical Impedance Spectroscopy (EIS), mechanical testing, such as tearing energy evaluation, Scanning Electron Microscopy (SEM), Fourier Transfer Infrared (FTIR), and thermal testing, such as Thermogravemetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). EIS measurements are typically carried out using a flat cell (similar to that reported previously by Aglan et al [6]) connected to a potentiostat. The impedance spectrum of the coated steel sample is fitted to that of an equivalent circuit model so that the impedances of the different elements can be estimated. Figure 1 displays the Randles equivalent circuit used in the current study. It is a simple model of a coated steel substrate in electrolyte solution. The resistors and capacitor in the equivalent circuit can be correlated with the physical features of the electrochemical system, such as the resistance from the solution, the charge transfer resistance (R_{ct}) of the coating, and the capacitance of the coating interface. The charge transfer resistance is a measure of the effectiveness of the coating to prevent corrosion.

Mechanical properties are normally studied by means of tensile testing of films from each coating material.

For elastomeric materials, the tearing energy concept is used rather than fracture toughness. The tearing energy, T, can be considered as a material property, characteristic of the resistance of an elastomer to tear propagation. The value of T is calculated as:

$$T = 2KaW_o \qquad (1)$$

where $K = \pi/\sqrt{\lambda}$ and λ is the extension ratio [9], a is the initial crack length and W_o is the strain energy density of the material found from the area under the load - displacement curve divided by the volume of the sample.

In the current study, VYHH and epoxy coatings were evaluated with and without nano reinforcement. The corrosion performance of these coatings was studied using EIS measurements. The tearing energy concept was invoked to rank the resistance of thin films manufactured from these solutions to tear propagation.
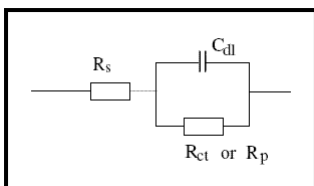

Figure 1. Randles Equivalent Circuit used with software to do EIS measurements [8].

2. MATERIALS AND EXPERIMENTAL
2.1 Materials

The materials used in this study were: Valspar Dura-Epoxy Finish (part A; alkyd glycidyl ether) mixed in a 2:1 ratio by mass with a hardener (part B; isophorone diamine), Union Carbide's VYHH, steel substrates, modified montmorillonite nanoclay (closite 30B). The nanoclay was supplied by Southern Clay Products Inc and was used as received. It has a specific gravity of 1.98 and was modified with methyl tallow bis-2-hydroxyethyl quarternary ammonium. The epoxy part A and B have boiling points of 330^oC and 204^oC, respectively and specific gravities of 1.14 and 1.03, respectively. VYHH has a specific gravity, T_g and molecular weight of 1.35, 72^oC and 72,000g/mol, respectively.

2.2 Experimental
2.2.1 Coatings Preparation and Procedures

The VYHH coating solution was prepared by dissolving VYHH powder in a previously optimized mixing ratio of solvents using a magnetic stirrer for about 48 hours. Nanoclay was added to the VYHH resin at the loadings of 0%, 0.5%, and 1.5% by weight. Neat and 1.5%wt clay / epoxy coatings were also prepared. The nanoclay was dispersed in the VYHH and epoxy resins by first mixing in a speed mixer followed by mechanical mixing. The edges and faces of the steel substrates were polished and degreased then left to dry for 24 hours. The samples were coated by a simple dipping procedure and inspected for defects to ensure an even coat. The average thickness of both polymer coatings was about 60μm± 10 μm. Four coated steel samples of each

formulation and three bare steel (as control) samples of each coating were submerged in the 5% NaCl solution. Two of each coated samples were left unsubmerged to be used for comparison with the submerged ones.

VYHH and epoxy films were cast in a 8"x8" mold with target thicknesses of 0.5 and 0.8mm, respectively. The films were then cut into dogbone samples having 60mm gage length x 12.7mm width and 140mm overall length. Four samples from each system were notched (5.1mm cut) and submerged with 4 unnotched samples in the 5% NaCl solution. Similar number of samples was left unsubmerged for comparison.

2.2.2 EIS Measurements

The EIS measurements were carried out on a Parstat 2273 manufactured by Princeton Applied Research. The voltage used was 10mV and the frequency range of the applied signal was 1MHz to 10 MHz. A one cm^2 portion of each coated sample was exposed to the 5%NaCl solution in the flat cell to determine the charge transfer resistance (R_{ct}) of the coating.

2.2.3 Mechanical Testing

The mechanical testing was performed on a Sintec 5D Material Testing System at a cross head speed of 7.62mm/min. The ultimate strength of the coatings was obtained from the unnotched specimens. The tearing energy, T, was calculated from the stress-strain relationship of the notched specimens according to Equation 1.

3. RESULTS AND DISCUSSION
3.1 EIS Measurements

EIS measurements were done on neat VYHH, VYHH/0.5%clay and VYHH/1.5%clay coated unsubmerged and submerged samples after 21 and 55 days of submersion in 5%NaCl solution. The data shown is the average of three tested samples. The unsubmerged neat VYHH and VYHH/0.5%clay samples had approximately the same R_{ct} values (23GΩ), while the VYHH/1.5%clay (42GΩ) was almost twice that of the neat VYHH. This shows that the addition of nanoclay have improved the corrosion resistance (R_{ct}) of the VYHH coatings because the nanoclay filled the voids and crevices in the matrix and prevent corroding agents from seeping through the coating. Also, since the clay particles are in the form of layers, the corroding agent has to travel a tortuous path to reach the substrate, which takes a longer time.

The resistance of the VYHH coatings as a function of time is shown in Figure 2. After 21 days of submersion, the resistances of VYHH/0.5%clay and VYHH/1.5%clay coatings were $4x10^3$ times larger than that of the neat coating. Therefore, the neat coating degrades/corrodes at a faster rate than the nano coatings. This means the rate of degradation was retarded by the nanoclay. However, at higher loadings of nanoclay and long exposure time the material becomes brittle and loses some of its cohesive capability.
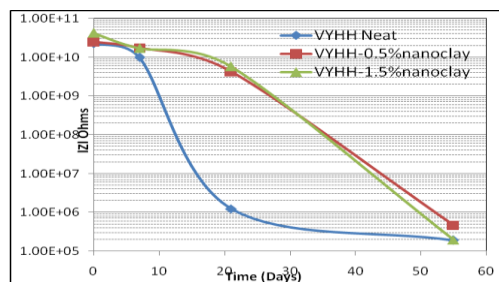
Figure 2. R_{ct} as a function of time for VYHH coated samples.

Figure 3 shows the R_{ct} values as a function of exposure time for the epoxy samples. The neat epoxy coatings deteriorate at a faster rate that the epoxy/1.5%clay. This verifies that the epoxy/1.5%clay sample offers better corrosion protection than the neat coating after submersion. This is attributed to the exfoliation of the clays in the coating which acts as filler for micro voids and crevices that are present in the neat epoxy coating, thus preventing the NaCl solution from seeping through the coating.

Table 1 shows a summary of the charge transfer resistances (R_{ct}) of all the coatings for the unsubmerged and submerged samples at different exposure time in 5%NaCl solution. There is a gradual decrease in the R_{ct} values over the 55 days exposure time for all the samples tested. The unsubmerged epoxy samples had higher (2 times) R_{ct} values than the unsubmerged VYHH samples. However, after 55 days submersion the VYHH coatings provide better corrosion protection.
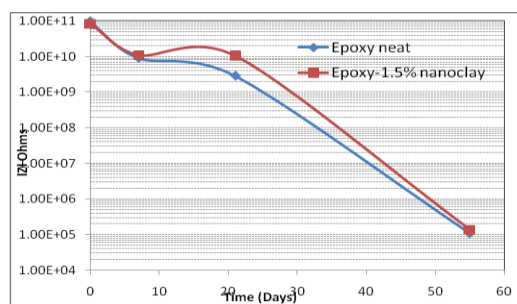

Figure 3. R_{ct} as a function of time for epoxy coated samples.

Rct Samples	Unsubmerged	Submerged	
		21 Days	55 Days
Bare steel	1.02 KΩ	320Ω	61Ω
Neat VYHH	22.8 GΩ	1.24MΩ	190 KΩ
VYHH/0.5%clay	24.7 GΩ	4.24 GΩ	462KΩ
VYHH/1.5%clay	42.2 GΩ	5.73 GΩ	196KΩ
Neat Epoxy	95.6 GΩ	2.87 GΩ	109KΩ
Epoxy/1.5%clay	82.9 GΩ	10.4 GΩ	136KΩ

Table 1. Charge transfer resistance (R_{ct}) of unsubmerged and submerged samples.

3.2 Mechanical Performance

Mechanical testing of the samples was performed on the notched and unnotched samples, both submerged and unsubmerged. The data reported in the current study is the average of three samples. The ultimate strength of the materials is obtained from the unnotched samples and the tearing energy is obtained from the notched samples. Table 2 shows a summary of these results. There is a slight increase in the ultimate strength of the VYHH samples, both unsubmerged and submerged as the nanoclay loading increases. The strain to failure shows a general decrease for both unsubmerged and submerged samples as the nanoclay loading increases. This suggests that the materials became more brittle with the addition of nanoclay. After 21 days of submersion there is a decrease in the ultimate strength of all the VYHH samples. However, the strain to failure of the VYHH samples increased significantly after submersion. This means that after submersion in 5%NaCl solution the material is toughened. The increase in toughness could be translated into better cohesive property of the coating, leading to enhanced corrosion protection.

The residual strength of the neat VYHH coating decrease at a faster rate than the nano coatings after 21 days submersion. Similar to the unnotched samples, the strain at peak stress for all the samples increased after submersion. This is reflected in the tearing energy calculations shown in Table 2. The tearing energy of the neat VYHH sample decreased by about 27% after submersion, while there was no significant change in the tearing energy of the VYHH/0.5%clay. The VYHH.1.5%clay showed a 9 % increase in tearing energy after 21 days submersion. Again, this suggests that the nano coatings are more durable (resistance to tear propagation) and have increased resistance to corrosion, as proven by EIS measurements. The nanoclay makes the coating material more viscous and improves the barrier properties and cohesiveness. However, it must be noted that if the coating is too viscous, proper wetting of the substrates can be hindered.

There was no significant change in the residual strength of the unsubmerged epoxy/1.5%clay sample over the neat material. However, after 21 days of submersion in 5% NaCl solution the epoxy/1.5%clay sample showed a 12.5% increase in the residual strength. The strain at peak stress for both neat epoxy and epoxy/1.5%clay increased about 65% after submersion. This correlates with the strain to failure of the unnotched samples. The tearing energy of the epoxy samples are also shown in Table 2. It is seen that the tearing energy of the neat material did not change after 21 days of submersion. However, the tearing energy of the epoxy/1.5%clay showed a 14% increase after 21 days submersion. This suggests that the nanoclay has improved the resistance of the material to tear propagation and also the cohesiveness of the coating after being submerged in NaCl solution. Again, this correlates with the EIS measurements, where after 21 days of submersion the epoxy/1.5%clay sample had higher corrosion resistance than the neat coating.

4. CONCLUSIONS

VYHH and epoxy coatings were evaluated with and without nanoclay reinforcement. The performance of these coatings was studied using EIS measurements and mechanical testing. The following conclusions can be drawn;

EIS techniques have been successfully used to evaluate the resistance of VYHH and epoxy nanostructured coatings after 55 days of 5%NaCl submersion. For both systems the nanostructured VYHH and epoxy offer better corrosion protection. Of all the samples evaluated, the VYHH/0.5%clay showed the highest R_{ct} value of 462KΩ after 55 days of submersion in NaCl solution. The unsubmerged epoxy samples had R_{ct} values more than twice the VYHH samples, but after submersion the epoxy coating deteriorate at a faster rate than the VYHH samples. In addition the neat coatings for both systems deteriorate much faster than the nano coatings.

The tearing energy of the neat VYHH coating decreased after 21 days submersion in 5%NaCl solution, while the VYHH nano coatings increased slightly. The neat epoxy showed no change in tearing energy after 21 days submersion, while the epoxy nano coatings showed a 14% increase after submersion. Further, both systems showed an increased strain to failure after 21 days of submersion in NaCl solution.

Sample/Exposure Time (Days)	Unnotched Samples		Notched Samples		
	Ultimate Strength (MPa)	Strain to Failure (%)	Residual Strength (MPa)	Strain At Peak (%)	Tearing Energy (KJ/m^2)
VYHH Neat/0 Days	3.27±0.22	287	1.94± 0.28	92.4	23.65
VYHH Neat/21 days	2.48±0.13	334	1.06± 0.07	113	17.31
VYHH/0.5%clay/0Days	3.52±0.16	233	1.38±0.14	70	18.27
VYHH/0.5%clay/21 Days	2.29±0.11	307	1.19± 0.07	92.7	18.10
YHH/1.5%clay/0Days	3.92±0.31	173	1.83± 0.13	35	17.13
VYHH/1.5%clay/21 Days	2.57±0.08	221	1.79±0.11	43	18.64
Epoxy Neat/0 Days	27.63±0.78	7	11.48±0.49	1.57	3.24
Epoxy Neat/ 21 Days	13.17±0.13	25.6	6.35±0.67	2.6	3.22
Epoxy/1.5%clay/0 Days	28.1±1.2	15	11.83±0.12	1.45	3.34
Epoxy/1.5%clay/21 Days	12.94±0.6	22.5	7.16±0.19	2.5	3.81

Table 2. Summary of mechanical performance of submerged and unsubmerged Epoxy and VYHH samples.

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