

# Electrochemical Impedance and Thermal Characterization of Nano-Reinforced Vinyl Chloride/Vinyl Acetate Coating

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## ABSTRACT

Multi-walled carbon nanotubes (MWCNT) were used to reinforce a poly(vinyl chloride/vinyl acetate) copolymer (VYHH) in order to evaluate barrier properties against corrosion. Both neat and nano-filled coatings were applied to steel substrates with two discrete target thicknesses: 30-40 microns and 60-75 microns. Coated and control samples were submerged in a tank with a 5% NaCl solution for 45 days. Electrochemical Impedance Spectroscopy (EIS) revealed that coating thickness plays a role in corrosion resistance. Differential Scanning Calorimetry (DSC) showed that the addition of MWCNTs improved the thermal stability of the VYHH. It was concluded that corrosion resistance is both a function of the MWCNT addition and the thickness of the coating.

*Keywords: nanostructured VYHH coatings, corrosion performance, electrochemical impedance spectroscopy, differential scanning calorimetry*

## 1 INTRODUCTION

Nano filled polymers are a promising alternative to traditional composites for effective barrier protection against degradation due to corrosion. In particular, the addition of multi walled carbon nanotubes (MWCNTs) in a variety of polymer matrices as reinforcement against corrosion have been studied [1-3]. Defects, cracks and voids are of particular concern in corrosion protection defense as these defects act as pathways that can promote diffusion of the electrolyte through the coating to the substrate. In a well dispersed system, the nanophase is available to fill in defects, nano-to-micro sized cracks and crevices, thus creating a more cohesive film. By filling the defects, the nanotubes may block existing pathways through the coating thickness, while retarding the advancement of new and partially formed pathways, thus improving the barrier properties of the host polymer to corrosion. Surface irregularities on the steel substrate also may be filled by MWCNTs in the polymer matrix. As the nanoparticles flow into and fill these crevices, the coated surface area increases, resulting in better adhesion of the coating to the substrate. A poorly adhered coating will blister and peel away from the substrate in spots, creating large channels for the electrolyte to contact the substrate [1, 3].

In addition to acting as filler, MWCNTs can improve upon the thermal and mechanical properties of a polymer matrix. It has been well documented that MWCNTs have superior properties, such as Young's modulus ( $\leq 1$  TPa),

tensile strength (20-100 GPa), thermal conductivity (6000 W/m/K), high aspect ratio and specific strength (48.5 MN x m/kg), among others. Ganguli, et al. studied the effect of loading rate and surface modification of MWCNTs on fracture toughness using a bifunctional epoxy as the polymer matrix. It was found that the addition of 0.15% MWCNTs, by weight, had an 80% improvement on fracture toughness for that system [4]. The addition of carbon nanotubes in a poly(vinyl alcohol) film yielded a 4.5 fold increase in the Young's modulus over neat poly(vinyl alcohol) film [5]. Ryan et al found that carbon nanotubes promoted crystallinity in the polymer, thus strengthening the matrix. He compared CNTs of different diameters and number of layers, and found that there is a correlation between crystallinity and mechanical performance, regardless of CNT geometries. Carbon nanotubes have also been effectively used as reinforcement against corrosion in electroplated coatings. It was found that the impedance of electro-disposed CNT-Zn to corrosion was consistently higher than electro-disposed neat Zn coating, indicating that the CNT-Zn coating is more resistant to corrosion [1].

Electrochemical Impedance Spectroscopy (EIS) is used as a measure of corrosion by correlating the amount of diffusion of metal ions from a specimen into an electrolyte to the measured resistance in the physical system once a current is applied. The measure of this diffusion from the metal into the electrolyte is called the charge transfer resistance ( $R_{ct}$ ) or impedance of the material to corrosion. EIS is a powerful tool in the investigation of coating effectiveness as a barrier to corrosion as a function of time, as the measurements are very stable and repeatable. The setup for EIS testing for corrosion takes into account the fact that electrochemical systems involving coated surfaces often behave like electrical circuits. In order to measure impedance the software of an EIS measurement must consider a circuit that best models the physical system. The Randles Cell is a simplified model of a physical system, consisting of a capacitor and two resistors, which can be used as an equivalent circuit to represent much more complicated systems [6]. EIS has been used to characterize the corrosion resistance properties in a variety of coatings [1-3,7-12]. Using EIS, it has been demonstrated that the number of layers or coating thickness of water-borne paint coatings has a positive impact on the magnitude of the impedance of the coating to corrosion [7]. EIS studies comparing the resistances of a polyurethane-nano Zn-O system and a polyurethane-micro Zn-O system showed that the impedance of the coating with the nano-sized particles was higher than that of the micro-sized particles, indicating

that the size of the particle is important to fill the defects formed during processing.

Poly (vinyl chloride-co-vinyl acetate) (PVC-co-PVAc) is currently used as a protective coating in a variety of applications. PVC-co-PVAc has low moisture absorption and thermal expansion. These are both desired attributes of a coating for corrosion protection in that the film will not swell and degrade simply as a result of being in an aqueous environment [13]. Differential Scanning Calorimetry (DSC) shows that the material is stable up to about 190°C and the amount of crystallinity, or, the amount of heat energy required to break the molecular bonds, is highly dependant on the type of solvent used in the formulation [14]. The addition of MWCNTs to PVC-co-PVAc are expected to improve upon the thermal properties of the material as thermal properties of CNT/polymer coatings are usually higher than their neat constituents, due to the high thermal characteristic of the CNTs.

In the present study, PVC-co-PVAc (VYHH) with and without MWCNTs are investigated for effectiveness as barrier for corrosion protection. In addition, the effect of coating thickness is also investigated. The prepared neat and nano-reinforced specimens were submerged in a 5% NaCl aqueous solution for a period of 45 days. The resistances of the aged samples to corrosion were determined experimentally using EIS and compared to the unaged specimens. Thermal characterization of the neat VYHH and nano VYHH coating was conducted using DSC.

## 2 MATERIALS AND EXPERIMENTAL

The VYHH used for this study was provided by Union Carbide and is formulated as an 86:14 copolymer, vinyl chloride to vinyl acetate. The polymer was received as a powder and was added at a 23.8% loading, by weight, to a 3.73:2.33:2.31 mixture of methyl isobutyl ketone (MIBK), xylene and toluene, respectively. The mixture was stirred on a magnetic stirrer for at least 24 hours, until the VYHH powder was dissolved. The multi-walled carbon nanotubes (MWCNTs) used in this study were provided by Ahwahnee Technologies. The diameter of the tubes is in the range of 2-15 nm, with a length of 1-10 μm and 5-20 layers. The nanotubes were added to the VYHH at a 0.1% loading rate by weight. In preparation for coating, stainless steel samples were cleaned and degreased with acetone. Once the substrates were cleaned and the coatings were prepared, the samples were carefully dipped once or twice in either neat VYHH or the nano-reinforced formulation. The target thickness for the single coated samples was 30-40 μm, while the target coating thickness for the twice coated samples was 60-75 μm. The samples were left to dry for 3 days. The specimens were then aged for 45 days in a submersion tank with a 5% NaCl solution.

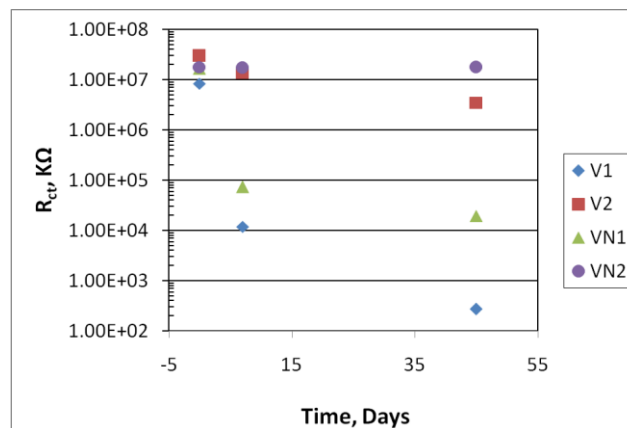
EIS measurements were taken using a potentiostat (Parstat 2273) with a flat cell. The testing was conducted over a frequency range of  $1 \times 10^6$  Hz to  $1 \times 10^{-2}$  Hz with 10 mV amplitude. Differential Scanning Calorimetry (DSC) was performed using a DSC Q1000 manufactured by TA

Instruments. The experiments were performed using a temperature range from 30°C to 300°C at 10°C/min under nitrogen.

## 3 RESULTS

### 3.1 EIS Measurements

Electrochemical Impedance Spectroscopy (EIS) was performed on bare steel as well as neat VYHH (V) and VYHH with 0.1% MWCNTs (VN) for one and two coated samples before submersion, at 7 and 45 days. These results are shown in Figure 1. After 45 days, the VN2 sample had an  $R_{ct}$  of 17.4 GΩ while the V2 sample had an  $R_{ct}$  of 3.5 GΩ. The higher impedance of the nano-reinforced VYHH coating indicates that the nano-reinforcement improves the ability of the coating to resist corrosion. The V1 and VN1 samples have  $R_{ct}$ s of 115 kΩ and 655 kΩ, respectively. This result is in agreement with the double coated samples, though the values are substantially different. The twice coated samples have  $R_{ct}$ s that are at least six orders of magnitude higher than the single coated samples after 45 days of aging.



**Figure 1. Charge transfer resistance versus time for neat (V) and nanoreinforced (VN), once and twice coated VYHH on steel substrates.**

The impedances for the single and double coated neat and nano-reinforced VYHH before submersion, at 7 and 45 days are given in Table 1. Before submersion, the V2 and VN2 samples have higher impedances than the V1 and VN1 samples, suggesting that there is a correlation between coating thickness and impedance. The average coating thickness for the double coated films is 76.3 ± 19.7 μm, while the one coat film average thickness is 27.3 ± 6.6 μm. The double coatings are more than twice as thick as the single coatings, on average. In a study on the corrosion-protection of paint coatings, one, two and three layered coatings were tested for their electrochemical impedance, and it was found that the thicker coatings consistently had higher impedance magnitudes over time [7]. Additionally, the nano-reinforced coatings exhibited a higher  $R_{ct}$  than the neat VYHH within their coating thicknesses. Apparently, the addition of CNTs

improved the barrier properties of the coatings by increasing the surface area interface between the coating and the substrate. The fact that the nano-reinforced samples (VN) consistently had higher impedances within their coating thickness relative to the neat samples (V) over time indicates that overall, the nano-reinforced coatings display a higher resistance to corrosion.

**Table 1. Impedances for coated and uncoated neat and nano VYHH before and after submersion.**

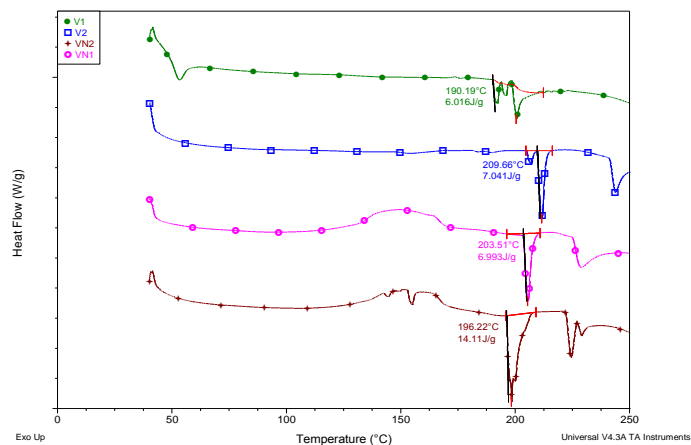
Rct, kΩ Samples	Unaged	Aged		
		7 days	45 days	Peeled after 45 days
Bare Steel	1.11	---	---	---
V1	8.3(10) <sup>6</sup>	11.8(10) <sup>3</sup>	115	0.42
VN1	16.4(10) <sup>6</sup>	72.5(10) <sup>3</sup>	655	0.94
V2	29.7(10) <sup>6</sup>	13.6(10) <sup>6</sup>	3.5(10) <sup>6</sup>	0.58
VN2	17.8(10) <sup>6</sup>	16.9(10) <sup>6</sup>	17.4(10) <sup>6</sup>	0.74

The data for the peeled steel and unaged steel are seen in Table 1. The unaged steel, peeled steel from aged VN2 sample, and from aged V2 sample impedances were measured to be 1106 Ω, 738 Ω, and 579 Ω, respectively. The peeled steel from aged VN1 and from aged V1 samples had impedances of 940 Ω and 420 Ω, respectively. The impedance of polished, unaged steel has been reported in the range of 1000-1500 Ω [3]. The peeled steels from the aged samples all have lower impedances than the bare steel, indicating that there was damage on the steel surface of the aged samples. These impedance values indicate somewhat less damage on the steel surface for the samples with coatings containing nanotubes.

### 3.2 Differential Scanning Calorimetry (DSC)

DSC thermograms of single and double coated neat and nano-reinforced VYHH are given in Figures 2 and 3 for unaged and aged samples, respectively. Endotherms due to crystalline melting are seen between 175°C and 210°C in both the aged and unaged samples (Figs 2 and 3). There was no crystalline melting endotherm in the DSC scans for the neat VYHH resin, indicating that the crystallinity was induced by the solvents used in the system [13]. The crystallinity is a result of the solvents evaporating at low temperatures. From Figure 2, it is seen that the enthalpies for the unaged V1, V2, VN1 and VN2 samples are 6.02 J/g, 7.04 J/g, 6.99 J/g and 14.11 J/g, respectively. The samples containing nano-reinforcements required the most energy to complete the endothermic transition within their coating thickness. MWCNTs used in polymer systems will often act as nucleation sites and to increase the percentage of crystallinity in polymer systems [15, 16]. The double coated nano-reinforced coating had the highest crystalline melt enthalpy, more than twice that of any of the other coatings, which suggests that there were more nucleation sites for

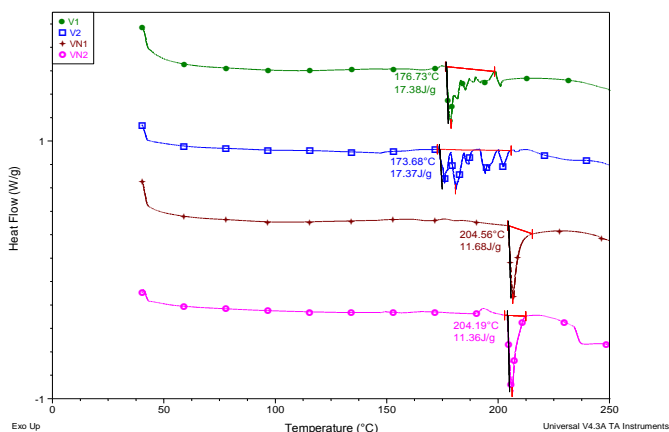
crystallization to occur due to the fact that the thicker coating created a more cohesive film with fewer defects than the single coated films. The single coated films had the lowest enthalpies, regardless as to whether or not nano-reinforcements were used. There was a difference of less than 1 J/g between the enthalpies of the single coated neat and nano films. Nevertheless, it should be noted that these crystalline melt energies are quite small and this system is largely amorphous.



**Figure 3. DSC thermogram for unaged single and double coated neat and nano-reinforced VYHH.**

After aging, the endotherms seen in the neat single and double VYHH coatings occurred on average 25°C lower than those seen in the thermograms of the unaged material, at 176.73°C and 173.68°C aged versus 190.19°C and 209.66°C unaged, for the one and two coated VYHH, respectively. In addition, the endotherms for the aged VYHH materials are very broad with several small peaks. The enthalpies for the aged coatings are 17.38 J/g, 17.37 J/g, 11.68 J/g and 11.36 J/g for the V1, V2, VN1 and VN2 coatings, respectively. After aging, it is seen that the neat VYHH required significantly more energy to complete crystallization melt than the unaged neat VYHH. During exposure, the NaCl solution diffused through the coatings whereby molecular species in the NaCl solution were able to freely interact with the VYHH molecule chains, causing relaxation in the chains. As a result, new crystalline regions were able to form at random interaction sites. The new crystalline regions are seen in the various new endotherms observed for the neat aged VYHH.

The endotherms for the aged one and two coated nano-reinforced VYHH can be seen at 204.56°C and 204.19°C versus 203.51°C and 196.22°C for the unaged one and two coated nano-reinforced VYHH, respectively (Figure 4). The peak crystalline melt temperature as a function of aging is mostly unaffected by addition of MWCNTs, remaining deep and narrow, which indicates that the molecular chains in the crystalline portion of the nano-filled



**Figure 4. DSC thermogram for single and double coated neat and nano-reinforced VYHH after 45 days of aging.**

coatings did not relax as was seen in the neat VYHH coatings. There was a decrease seen in the enthalpy of the aged double nano coatings from 14.11 J/g to 11.36 J/g. This result correlates with EIS data for the peeled nano coated steel indicating that there was some loss in  $R_{ct}$  with exposure. To a lesser extent, differences seen in enthalpies may also be a function of the randomness of the distribution and number of nucleation sites at the MWCNTs. Since both peak crystalline melt temperature and total crystalline melt enthalpy of the nano coatings were largely unchanged as a result of exposure, the introduction of MWCNTs in VYHH creates a coating with better barrier properties than neat VYHH.

#### 4. Conclusions

Neat and nano VYHH coatings were formulated and applied to steel substrates. The coated samples were submerged in a 5% NaCl solution for a period of 45 days. The following conclusions can be drawn:

The nano-reinforced VYHH had higher impedance to corrosion than the neat VYHH throughout the 45 day duration of the experiment. The impedances of the single coatings are lower than that of the double coatings, indicating that there is a correlation between coating thickness and corrosion resistance. The nano VYHH coatings had the highest impedance within both coating thicknesses.

DSC thermograms revealed that the peak melt temperature of the neat VYHH decreased by an average of 25°C after aging and the transition occurred over a broad temperature range. There was no change in the peak melt temperature in the nano coatings, and crystalline melting occurred in over a very narrow temperature range. Molecular chain relaxation occurred in the neat VYHH, causing the formation of new crystalline entities, while there was no evidence of chain relaxation in the nano-reinforced coatings. It is believed that chain relaxation is a result of diffusion of the NaCl solution through pathways in the film, and that the nanophase restricts the interaction between the molecular species in the NaCl solution and the polymer chains.

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