APPLIED GRAPHENE MATERIALS

Anticorrosive Performance of Novel Water based Systems using Graphene Nanoplatelets

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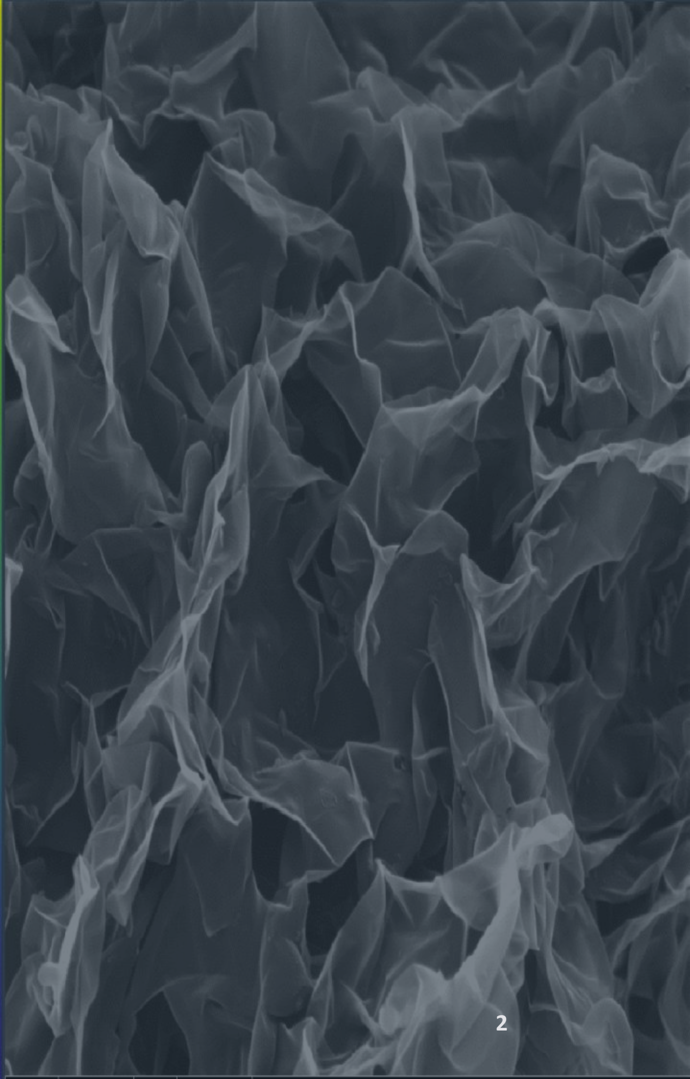
A DECADE OF INNOVATION

Introduction



Introduction

- Graphene as a 2D nanomaterial has been extensively researched as a new additive to improve barrier performance, **reducing corrosion** and **extending service life**.

- The authors have previously demonstrated significant uplifts in anticorrosive performance in solvent based coatings through the use of graphene nanoplatelets (GNPs), presenting **new opportunities** for improved protective coatings with extended service life.

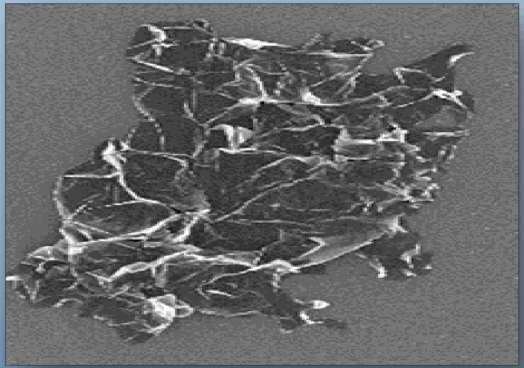
- Water based coating development remains a key focus for industry formulators where there is an ongoing effort to **reduce the release of volatile organics** and achieve comparable anti-corrosion performance to that seen in solvent based systems.

- For this work, report on the coating performance benefits when GNPs are incorporated into a **water based epoxy primer**, with a particular focus on improving anticorrosion performance.

Introduction

Graphene Nanoplatelets (GNPs)

- Thin, crumpled nanoplatelet sheets.
- Very low density, high surface area and high aspect ratio enabling enhanced corrosion protection.
- Excellent barrier properties.
- Typical loading levels 0.5-1% by weight in dispersion.
- GNP loading levels in final formulations typically 0.025 to 0.1%.

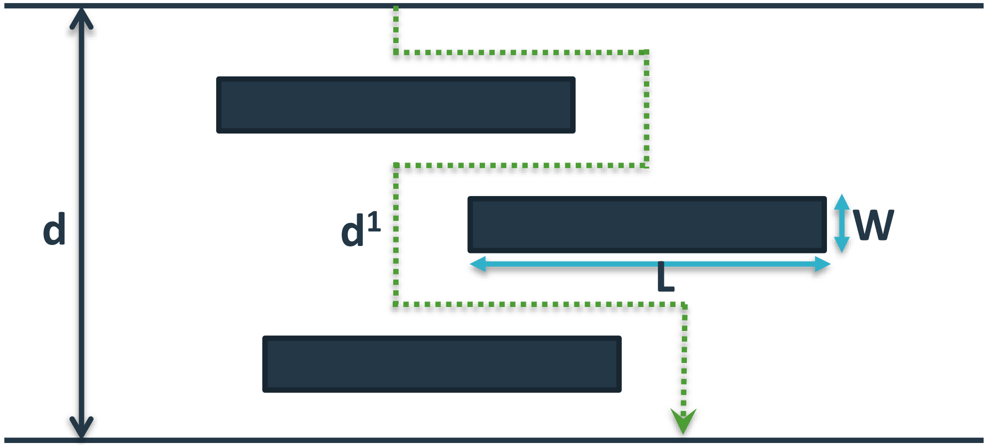


- Graphene nanoplatelets manufactured using a proprietary ‘bottom-up’ process
- Graphene is supplied in a formulated dispersion format to enhance stability and ease of use.

GNP – Mechanism of Barrier Enhancement

How GNPs work as a Barrier - Nielsen Theoretical Model

Effect of Platelet Size and Concentration on Permeability



Total path of a diffusing gas

$d^1 = d + d*L*V_f/2W$

- **d = coating thickness**
- **L = length of platelet**
- **W = width of a single platelet**
- **V_f = volume fraction of platelets**

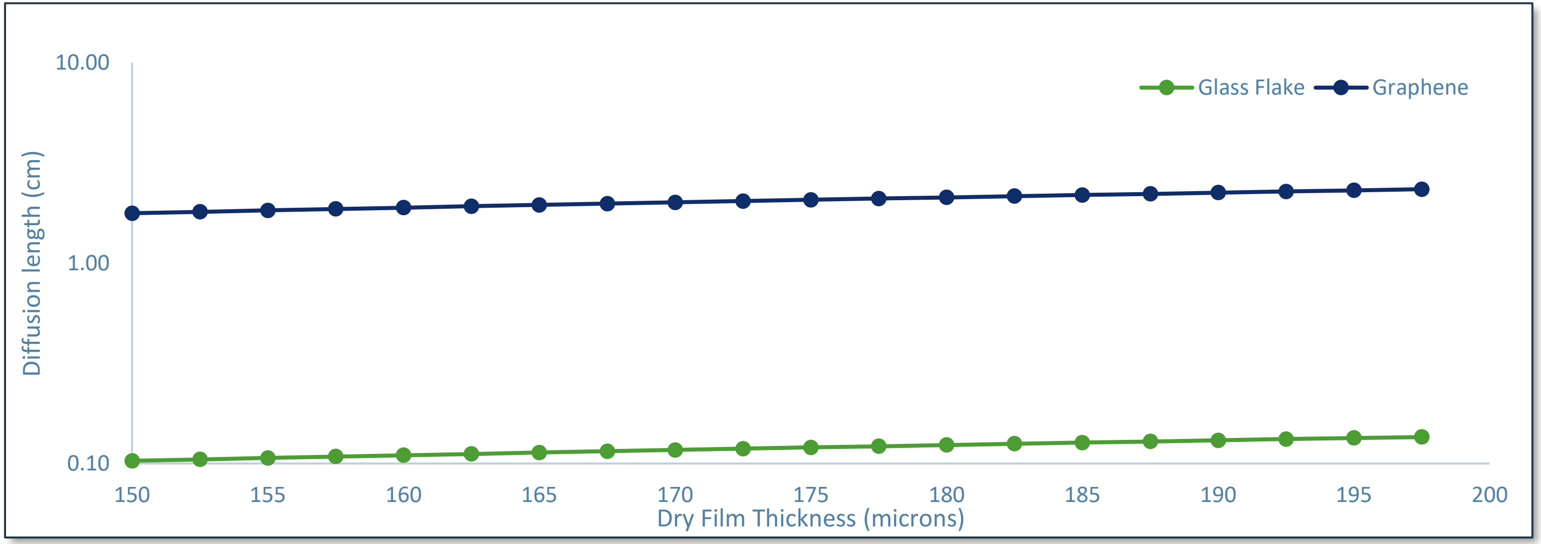
Tortuosity factor

$T = d^1/d$

$= 1 + L*V_f/2W$

Dispersion is key to achieving platelet distribution within the system

Barrier Performance Comparison to Glass Flake – Neilsen Model



Based on glass flake loading of 10% and GNP loading of 0.025%

- Graphene provides approximately 20 times the diffusion length within a coating when compared to glass flake.
- Graphene offers the potential for increased diffusion lengths at lower dry film thickness.

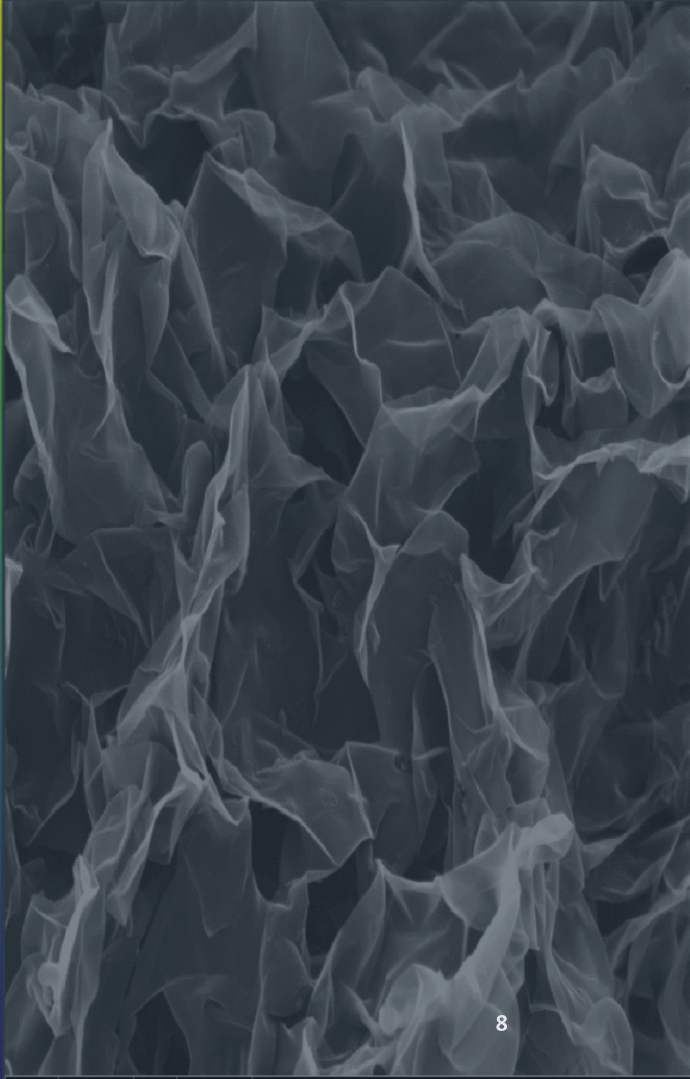
Objectives

Demonstrate coating performance benefit when GNPs are incorporated into a waterbased epoxy primer, with a **particular focus on improving anticorrosion performance**:

- Demonstrate extension of life using traditional anticorrosive test methods such as neutral salt spray and prohesion.

- Investigate and report on potential mechanism through the use of electrochemical impedance spectroscopy.

Experimental



Test Program

An epoxy prototype base was formulated to be representative of a typical **water-based epoxy primer**.

A range of tests were then carried out to determine suitability of the graphene enhanced waterbased coatings for use as **anticorrosive primers**, namely:

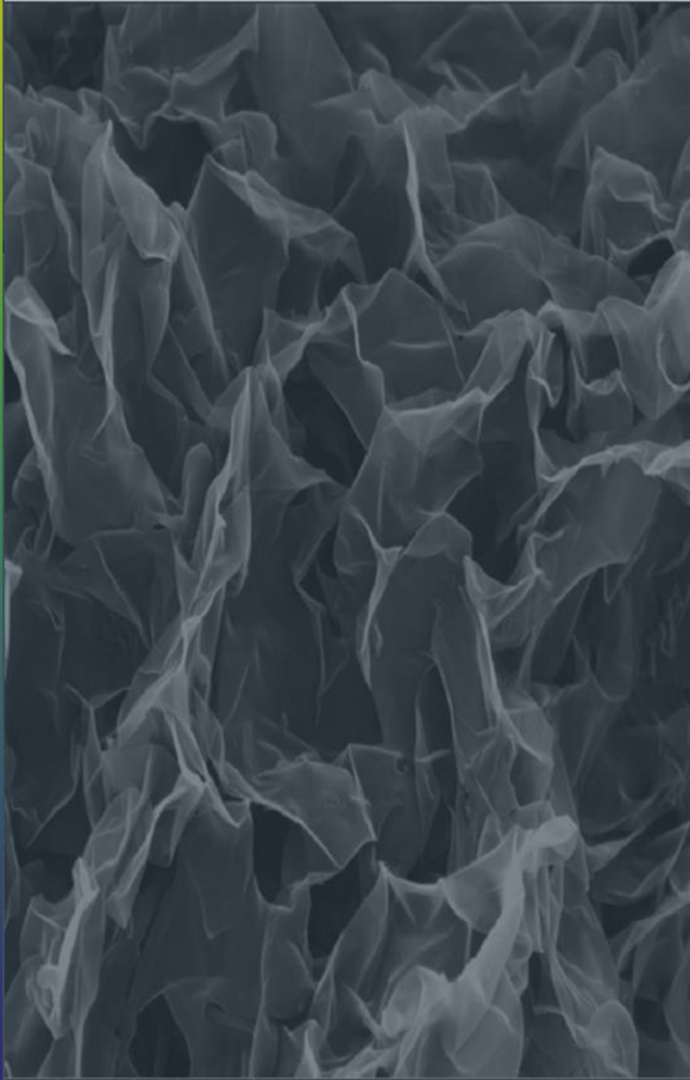
- Neutral salt spray – ISO 9227
- Prohesion Testing - ASTM G-85 Annex 5
- Electrochemical Impedance Spectroscopy (EIS)

Substrate	Cold Rolled Steel
Dimensions	152 mm by 101 mm
Preparation	Grit blasting to SA2-1/2, acetone degreases
Grit	Irregularly shaped chrome/nickel shot
Application	Steel Drawdown Bar (300 µm)
Coating Thickness	DFT 80 – 100 µm
Curing	7 Days at Room Temperature (25 ^{o}C)

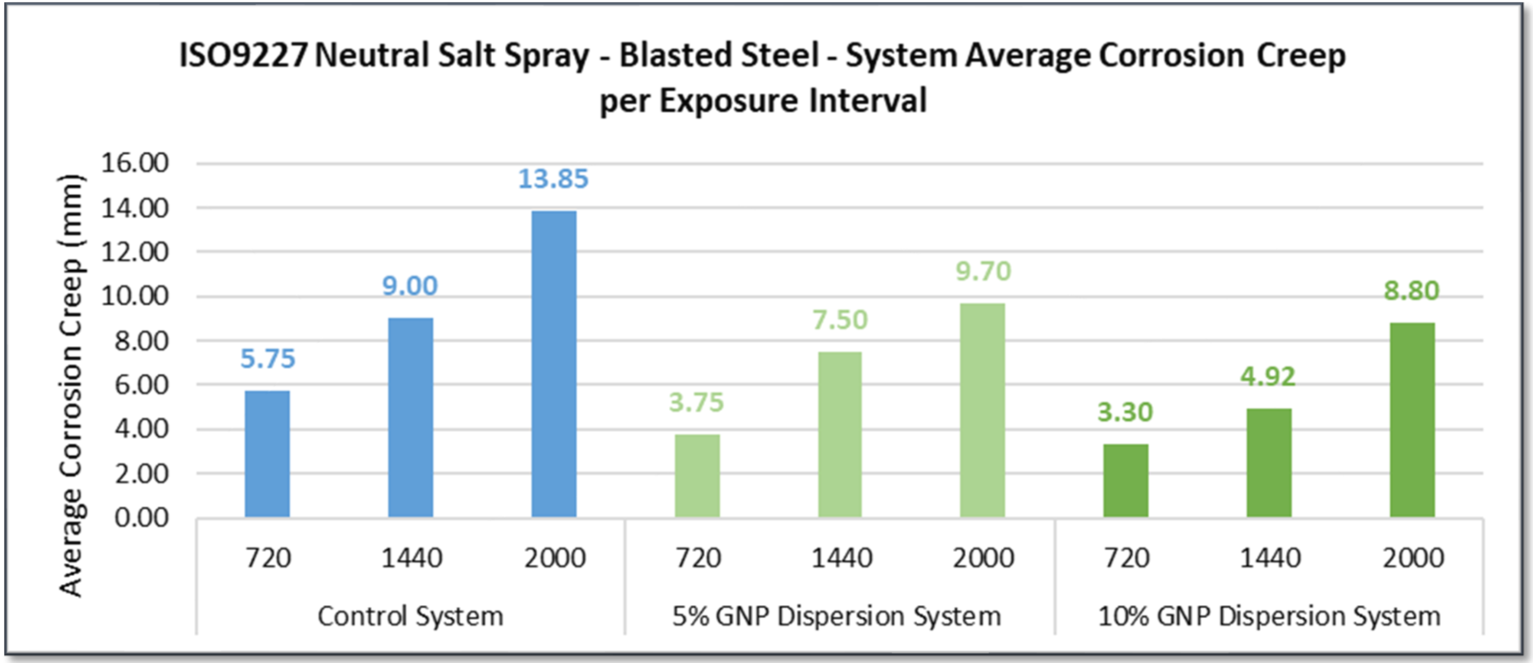
Formulations

Part A: Epoxy Base				
Item	Raw Material	Weight%		
		Control System	5% GNP Dispersion System	10% GNP Dispersion System
1	Waterborne Epoxy (57% WA)	**34.45%**	36.35%	38.02%
2	Dispersing Agent	**1.34%**	1.41%	1.48%
3	Defoaming Agent	**0.26%**	0.27%	0.28%
4	Talc	**4.81%**	5.07%	5.31%
5	Ti Pigment	**16.91%**	12.14%	7.62%
6	Yellow Fe Pigment	**0.21%**	0.15%	0.10%
7	Black Fe Pigment	**0.69%**	0.49%	0.31%
8	Barium Sulphate	**13.22%**	9.49%	5.96%
9	Water	**11.85%**	12.51%	13.08%
10	Thickener	**0.60%**	0.63%	0.66%
11	GNP Dispersion	**-**	**5.00%**	**10.00%**
12	Flash Rust Inhibitor	**1.00%**	1.00%	1.00%
Part B: Curing Agent				
13	Waterborne Curing Agent (55% WA)	**13.12%**	13.85%	14.48%
14	Water	**1.54%**	1.64%	1.70%
	Total =	**100.00%**	100.00%	100.00%
Note: Weight% are based on the full system loading, Part A + Part B				
PVC		**31.47%**	31.47%	31.48%
Graphene Loading		0.00%	**0.025%**	**0.05%**

Neutral Salt Spray Testing – ISO 9227



Neutral Salt Spray – ISO 9227



The inclusion of graphene showed a reduction in corrosion creep (~30%) for both graphene modified systems, at loading levels of 0.025-0.05%

Neutral Salt Spray - continued

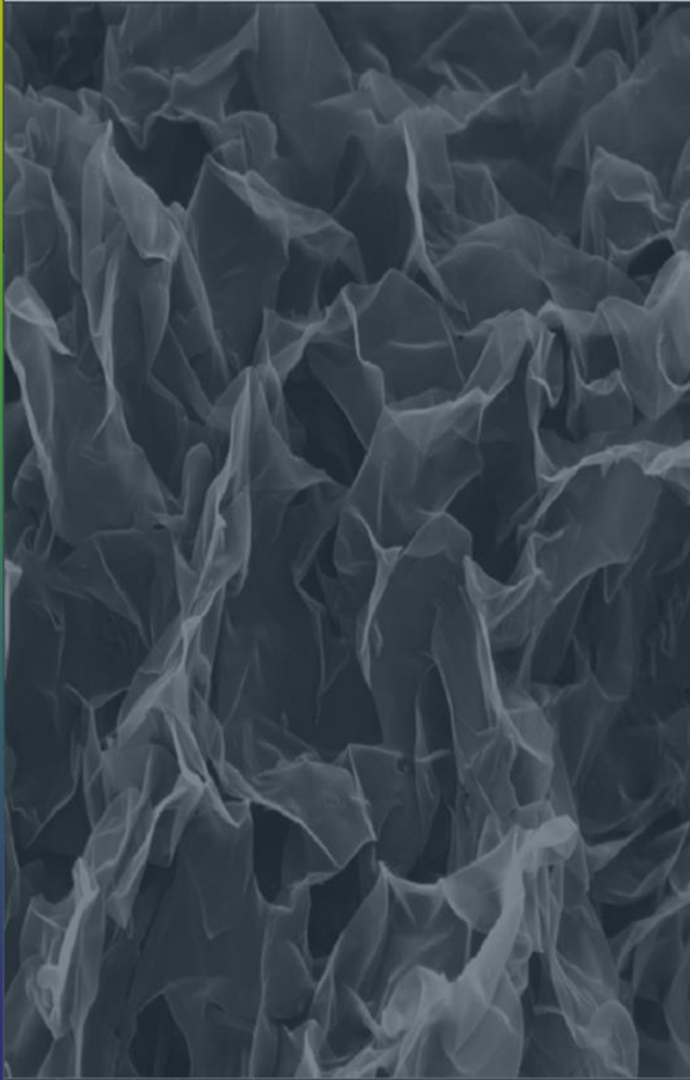
Blistering Assessment at 2000 Hours

System	Blister Rating						
	Micro	Size 1	Size 2	Size 3	Size 4	Size 5	Location
Control System	2	2	2	1	1	0	Widespread
	4	3	3	2	0	0	Widespread
5% GNP Dispersion System	0	0	1	2	0	0	Widespread
	0	0	0	3	0	0	Widespread
10% GNP Dispersion System	0	0	1	0	0	0	Widespread
	0	0	1	1	0	0	Widespread

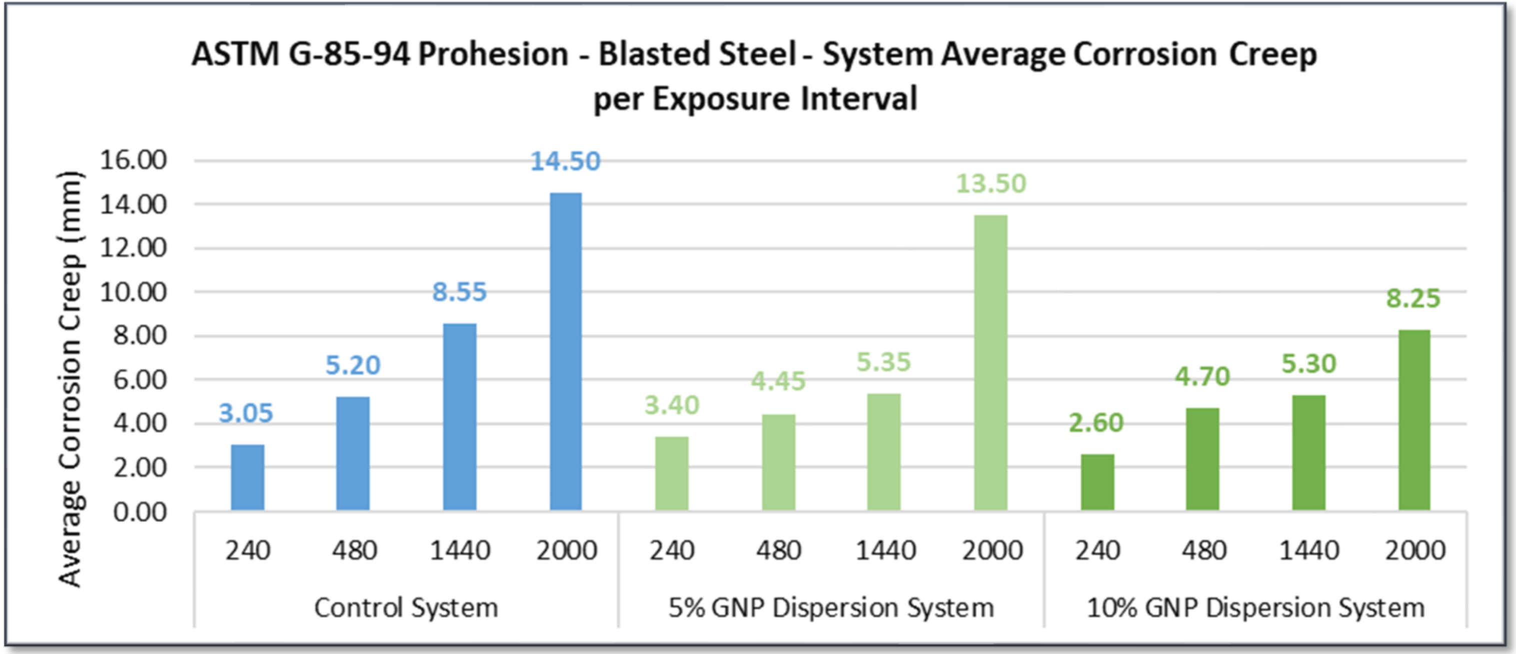
After 2000 hours on test, coatings containing graphene showed a **lower tendency to blister**.

Prohesion Testing

ASTM G85 Annex 5



Prohesion Testing – ASTM G85-94 Annex 5



A reduction in creep was noted with inclusion of graphene, particularly at the higher loading (~40%).

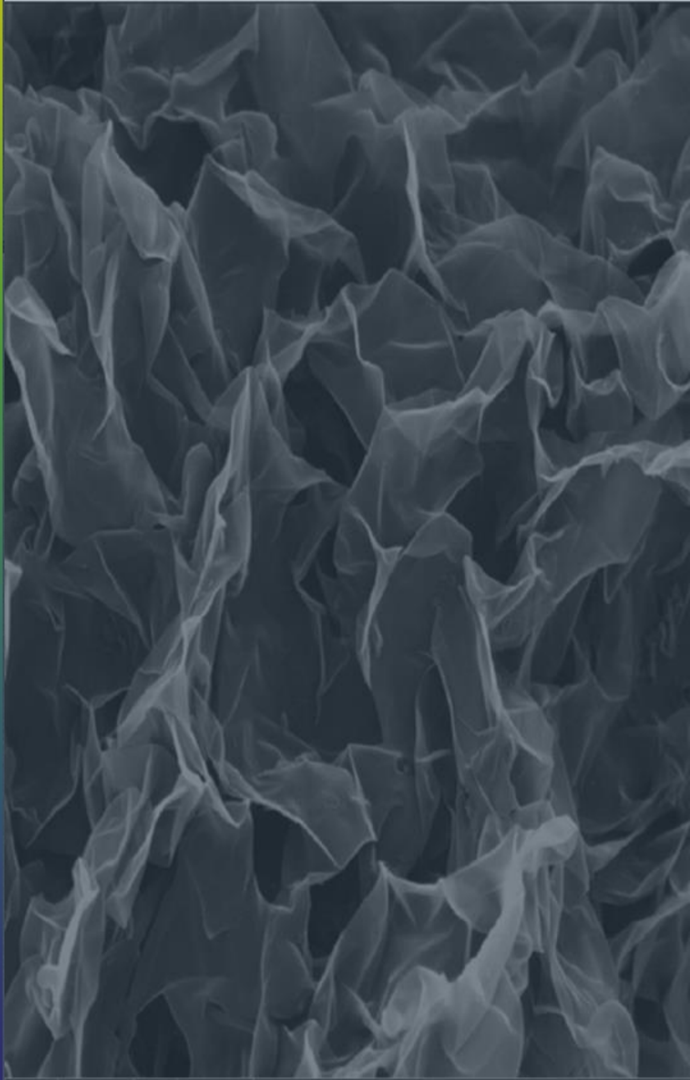
Prohesion Testing – continued

Blistering Assessment at 2000 Hours

System	Blister Rating						
	Micro	Size 1	Size 2	Size 3	Size 4	Size 5	Location
Control System	0	0	0	0	0	4	Around scribe
	0	0	3	1	0	0	Around scribe
5% GNP Dispersion System	0	0	2	2	0	0	Around scribe
	0	0	0	3	0	2	Around scribe
10% GNP Dispersion System	0	0	4	0	0	0	Around scribe
	0	0	2	0	0	0	Around scribe

Blisters appeared predominantly at the scribe but did not show any particular trend across the system.

Electrochemical Impedance Spectroscopy (EIS)

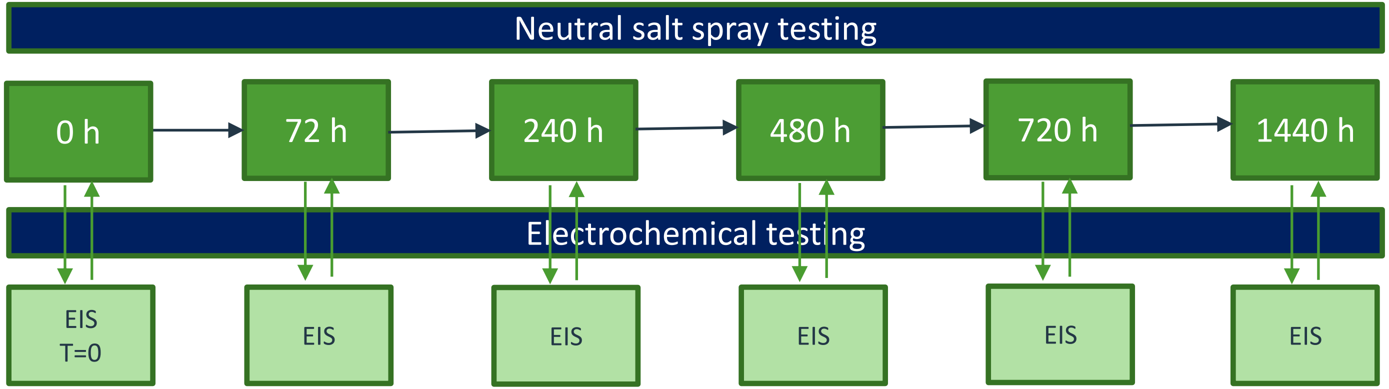


Electrochemical Testing

Equipment setup

- Measurements recorded using a potentiostat in conjunction with a multiplexer
- The test area of the working electrode was 14.6 cm^2 and run using a 3.5 wt% NaCl electrolyte
- An AC perturbation of 10 mV was applied across the samples, with a zero volt DC bias, over a frequency range of 1 MHz to 0.05 Hz
- Combined NSS/EIS Test Method
- Samples initially tested before being placed under NSS (T=0) and then retrieved from NSS at time intervals for subsequent testing

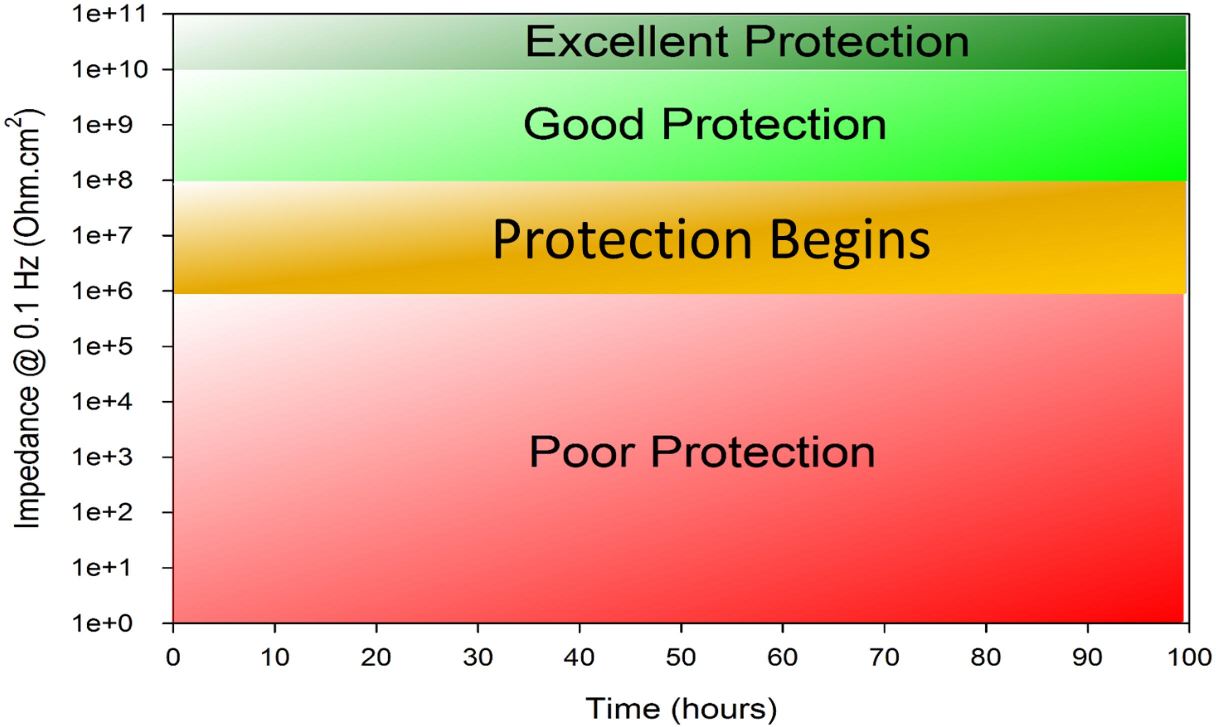
Combined Testing



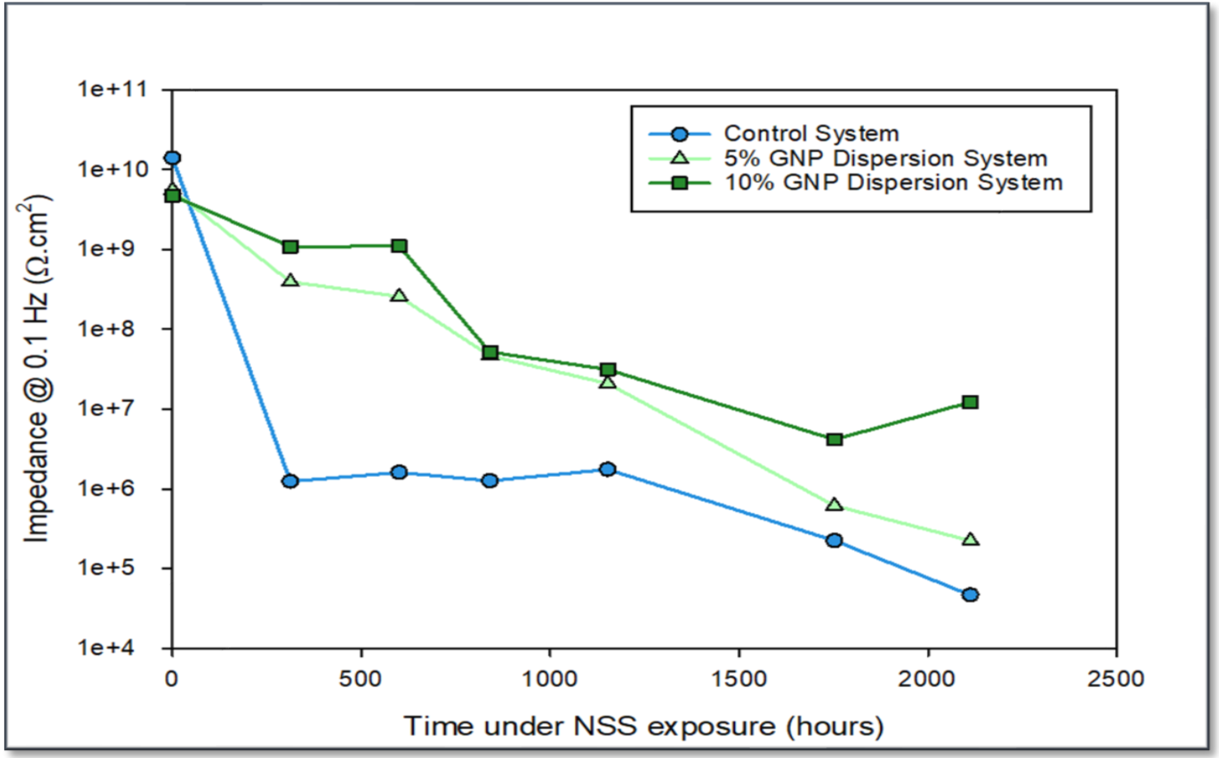
Dual testing approach

- Combined tests are complimentary to each other since EIS can determine relatively small changes within the coating e.g. with respect to water uptake prior to any visible coating changes noted from the examination of the test panels
- The test conditions of NSS are more realistic and accelerative compared to simply submerging the sample in NaCl solution, under ambient conditions, as is usually done during prolonged EIS studies within the paint test cell
- Test data from EIS and salt spray test results may also be used to corroborate coating performance.

EIS – Protection Regions



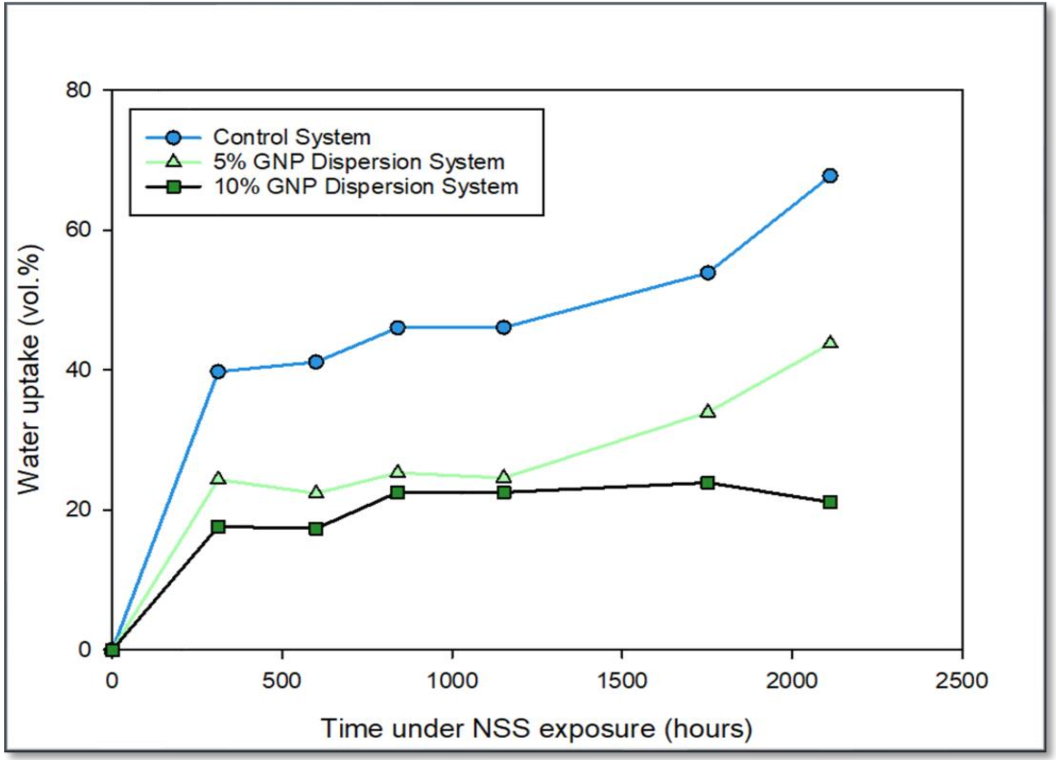
EIS Testing – Impedance



The higher impedance coating was that of the higher GNP loaded sample, followed by the lower GNP loaded sample.

This suggests both samples possess better barrier properties over the control sample.

EIS – Water Uptake

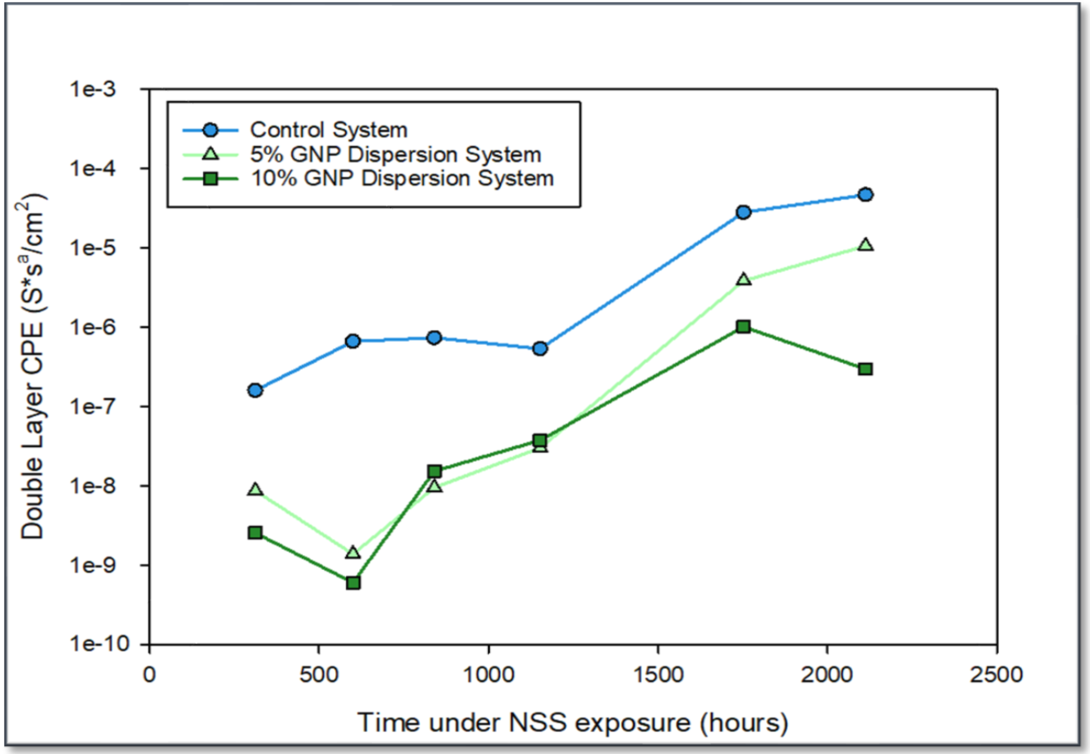


Over the duration of the combined EIS/NSS test, the graphene free control showed a water uptake just under 70% by volume.

In contrast, both of the graphene enhanced coatings showed significantly less water uptake. With the higher loading showing a water uptake around 20%.

This further re-enforces the theory of a barrier mechanism.

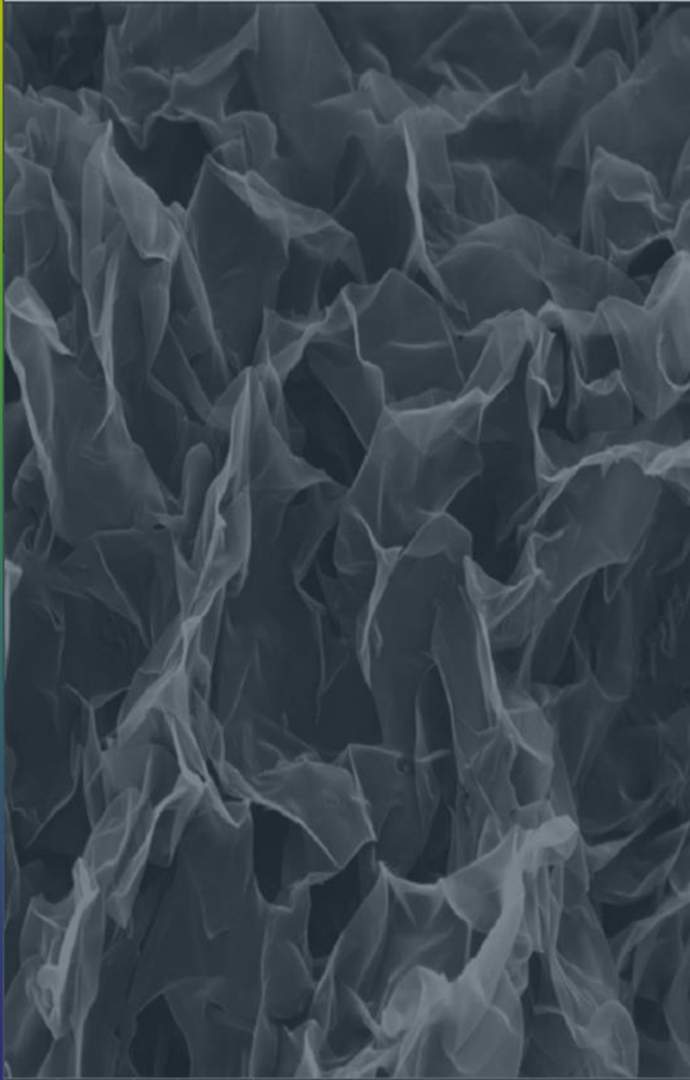
EIS – Double Layer Capacitance



In order to further examine the coated panels for evidence of electrolyte at the coating/substrate interface, equivalent circuit modelling was carried out.

Greater double layer CPE values indicate a larger presence of electrolyte at the interface, and, potentially, greater levels of corrosion.

Summary and Conclusions



Summary

The addition of **Graphene Nanoplatelets (GNPs)** into a water-based epoxy coating demonstrated improvements in anticorrosion performance as shown through various methods:

i. Reduction in creep and blistering on NSS testing up to **30%** improvement.
ii. Reduction in creep on prohesion testing, by up to **40%** for the higher loading.
iii. Significantly **higher impedance** values over 2000 hours of testing
iv. **20 to 40%** reduction in water uptake of the graphene enhanced coatings.
v. **Lower levels** of electrolyte at the substrate / coating interface as detected by double layer capacitance testing.

In all cases, the higher loading of graphene gave the best performance.

Conclusions

- Dispersions of graphene nanoplatelets **significantly improve the performance** of a water-based anti-corrosion coating.
- As the coatings industry moves towards **sustainable** and **environmentally beneficial** technologies, the ability to formulate waterbased coatings with a potential to match traditional solvent-based coatings becomes critical.
- Graphene nanoplatelets offer an additional formulating tool in combination with traditional additives to achieving high levels of **anticorrosion** performance using sustainable technologies such as waterbased epoxies.
- Furthermore, GNP dispersions offer the coatings formulator a greater **extension of coatings life** to develop more water-based products.

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