APPLIED GRAPHENE MATERIALS

Waterborne Epoxy Coating – Lifting performance for tomorrow

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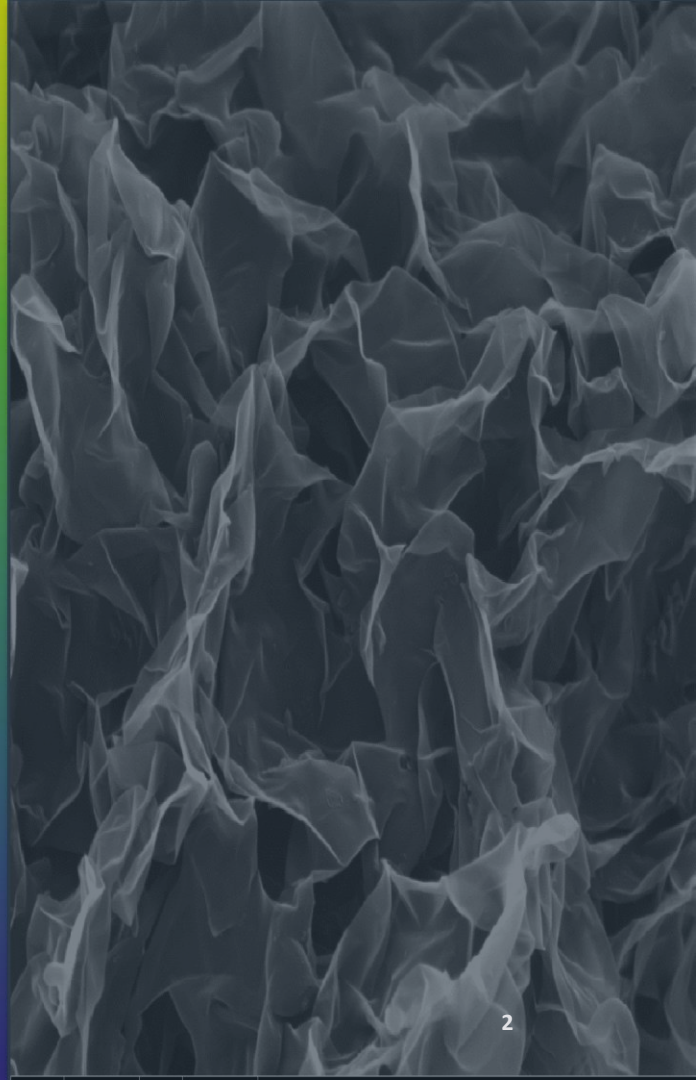
2021 ACA Coatings Tech Conference

appliedgraphenematerials.com

Introduction & Objectives



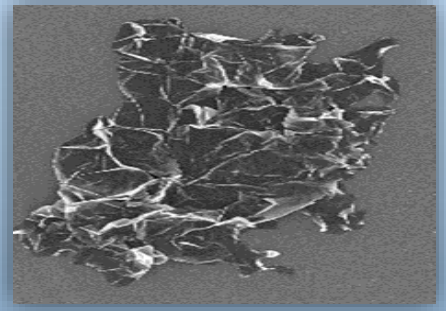
Introduction

- Graphene, as a 2D high aspect ratio material, 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, we 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 nano-platelet sheets
- Very low density, high surface area and high aspect ratio enabling enhanced corrosion protection
- Excellent barrier properties
- Typical graphene nanoplatelet loading levels in dispersion of 0.5% to 1.0% by weight
- Loading levels of AGM's dispersions in final coating formulations typically between 2.5% to 10% by weight of this dispersion

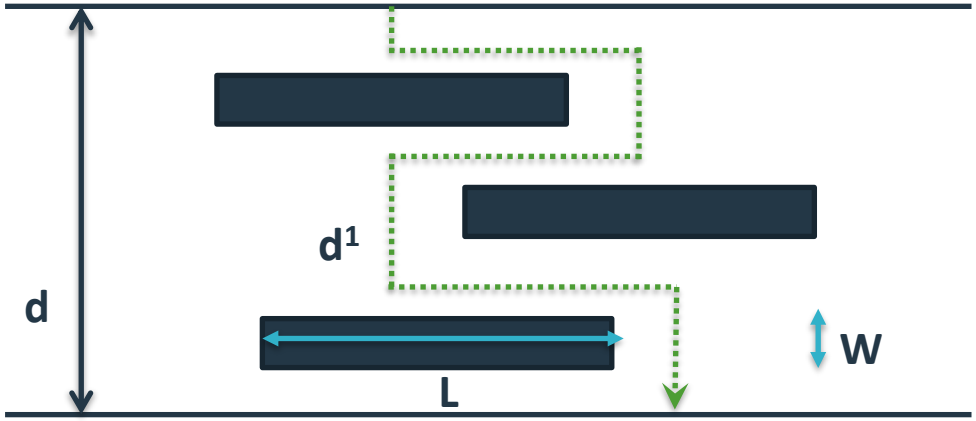


- Graphene nanoplatelets manufactured using a proprietary 'bottom-up' reaction process
- Graphene is supplied as a formulated dispersion to enhance stability and ease of use

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

$T = d^1/d$

$= 1 + L*V_f/2W$

Comparing a 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.
- Dispersion is key to achieving platelet distribution within the system

Objectives

1. Overcome the challenges that Graphene Nanoplatelet powders present when developing **optimized**, **stable** and **easy to incorporate** water based dispersions fit for use in industrial paint systems

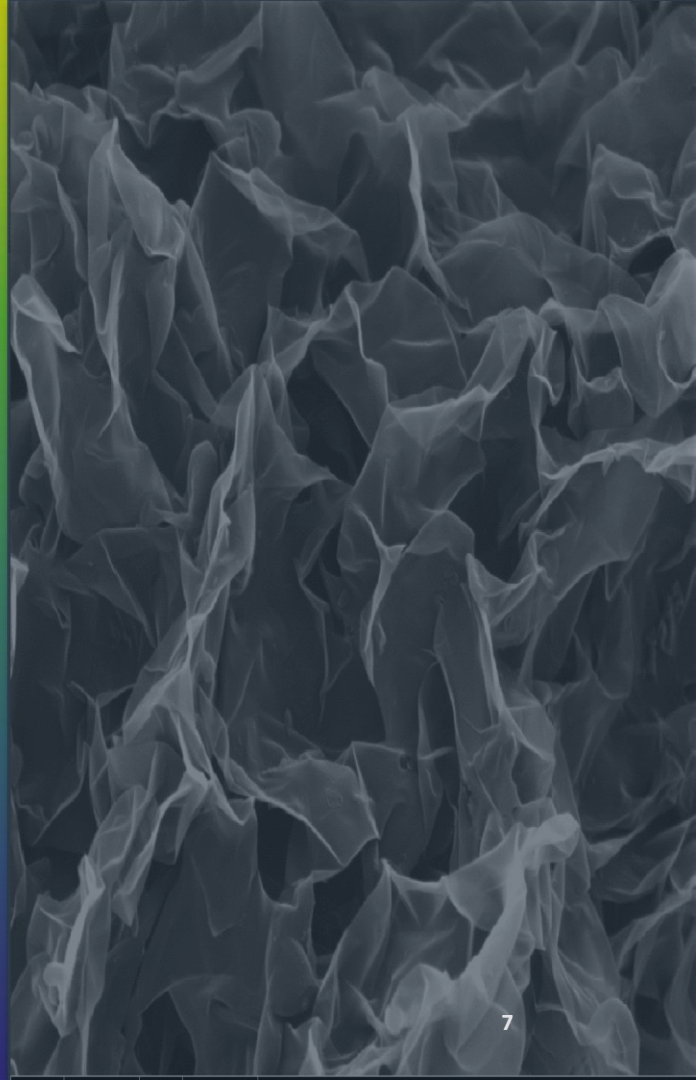
2. Outline the advantages of high quality stable dispersion that facilitate performance benefit when incorporated into a water based epoxy primer, focusing on **improving anticorrosion performance**

3. Demonstrate potential for extension of life using both:

    I. the industry standard anticorrosive test method, neutral salt spray(NSS) assessment

    II. and further developing the performance mechanism through the use of electrochemical impedance spectroscopy(EIS)

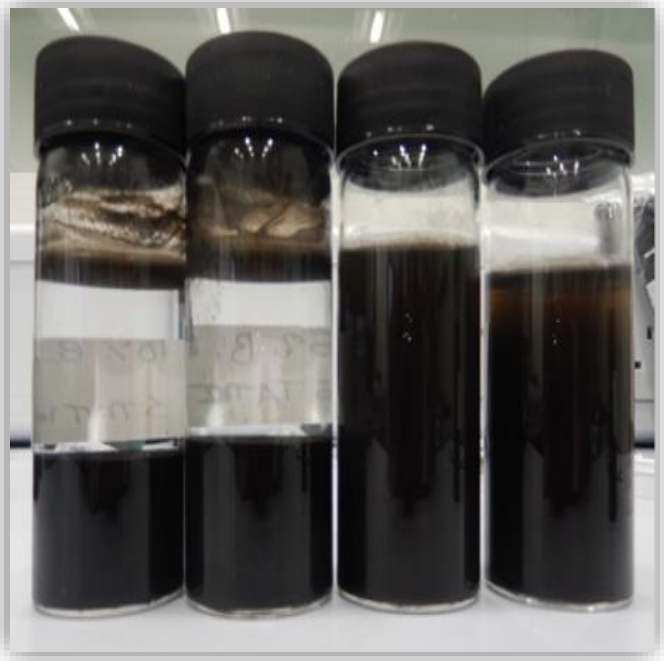
Aqueous Dispersion of Graphene



Challenges of Dispersing Graphene

Water Based Dispersion – the Challenges…

- Dispersion of graphene nanoplatelets **is** challenging for a number of reasons:
  - Carbon based pigments/materials have an affinity for each other and will tend to **flocculate**, **agglomerate** and **aggregate**
  - Furthermore, Graphene nanoplatelet, when unstabilized have a tendency to **"re-stack"** with the nanoplatelets agglomerating across the platelets lateral surface resulting in an **increase in the thickness** of the graphene nanoplatelet sheets
  - The absence of **polar hydrophilic groups** on the surface of the graphene nanoplatelets also makes dispersion and stabilization in water based systems a further challenge
  - Maintain the nanoform for regulatory considerations



Water Based Dispersion of Graphene

Water Based Dispersion – The Challenge downstream

- Dispersion of graphene nanoplatelets in water-based systems can be problematic, poor quality dispersions can result in a significant number of issues including:
  - **in-can instability** of the dispersion on storage
  - large loading levels of **surfactant** are needed, significantly impacting the usability of the dispersion and **negatively effecting** the hydrophobicity of final coating
  - **incompatibility** with test coating systems, cause potential incorporation issues during addition of the dispersion to the coating and could even **impact the longer term in-can stability** of the coating system
  - destabilization can result in the dispersion particle size increasing over time due to **agglomeration** and **aggregation**. This is likely to result in a **drop in performance** compared to a dispersion with a stable and optimized PSD

Water Based Dispersion of Graphene

Water Based Dispersion – The Challenges…

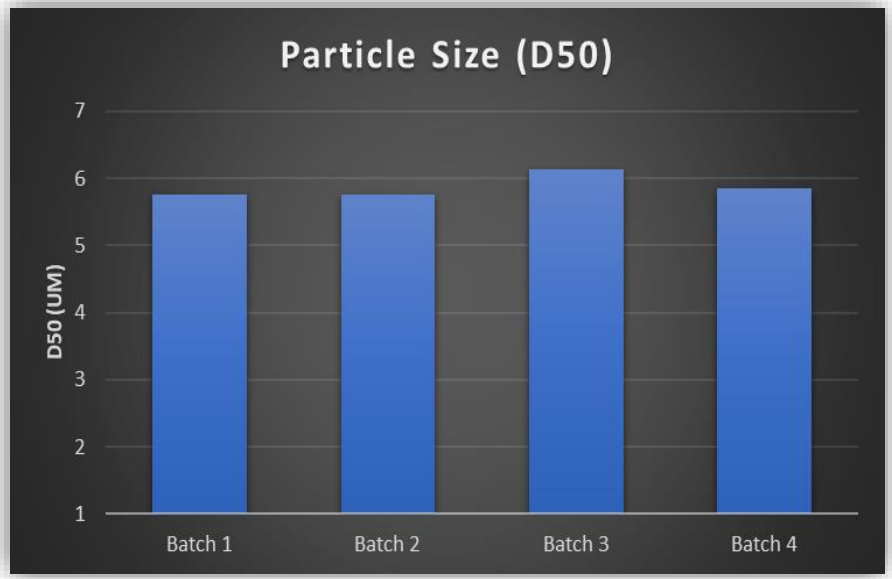
- AGM has developed novel water based graphene nanoplatelet dispersions which are:
  - **Easy to handle** and **incorporate** into existing industrial systems
  - **Long-term stability** of standard dispersion products
  - **Optimised dispersion** properties designed for final application
  - **Enabling** industry to benefit from the potential of graphene in a simple, safe and easy to formulate way.
- AGM's development enables the efficient use of graphene's inherent barrier properties to now be widely utilized in water based system
- This presents new opportunities for improved water based protective coatings with extended service life

Dispersion Quality

Water Based Dispersion – The Solution…

- AGM has developed a resin-supported stabilized dispersion
- This aqueous dispersion has reproducible quality and with excellent stable, showing no agglomeration and sedimentation effects
- Across 4 batches, repeatable density, viscosity and particle size distribution

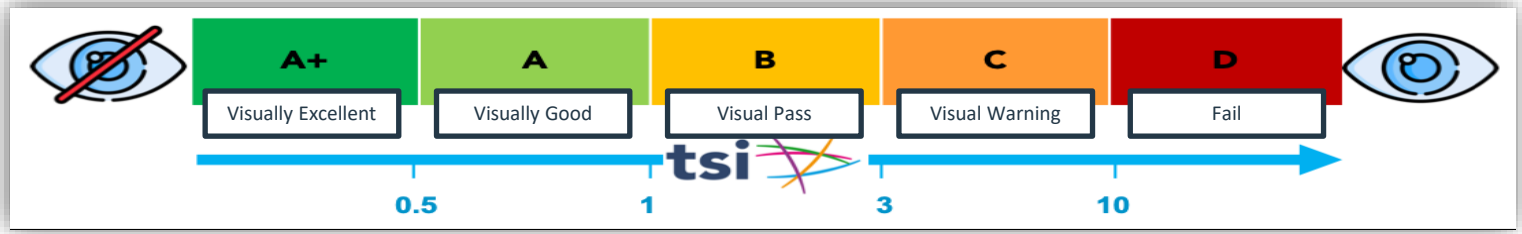
	Density (g/ml)	Viscosity (Pa.s)	D10 (µm)	D50 (µm)	D90 (µm)
Batch 1	1.01	1.19	2.11	5.76	13.57
Batch 2	1.02	1.02	2.11	5.76	13.57
Batch 3	1.02	1.15	2.17	6.13	16.13
Batch 4	1.02	1.16	2.11	5.85	13.7



Stability Testing

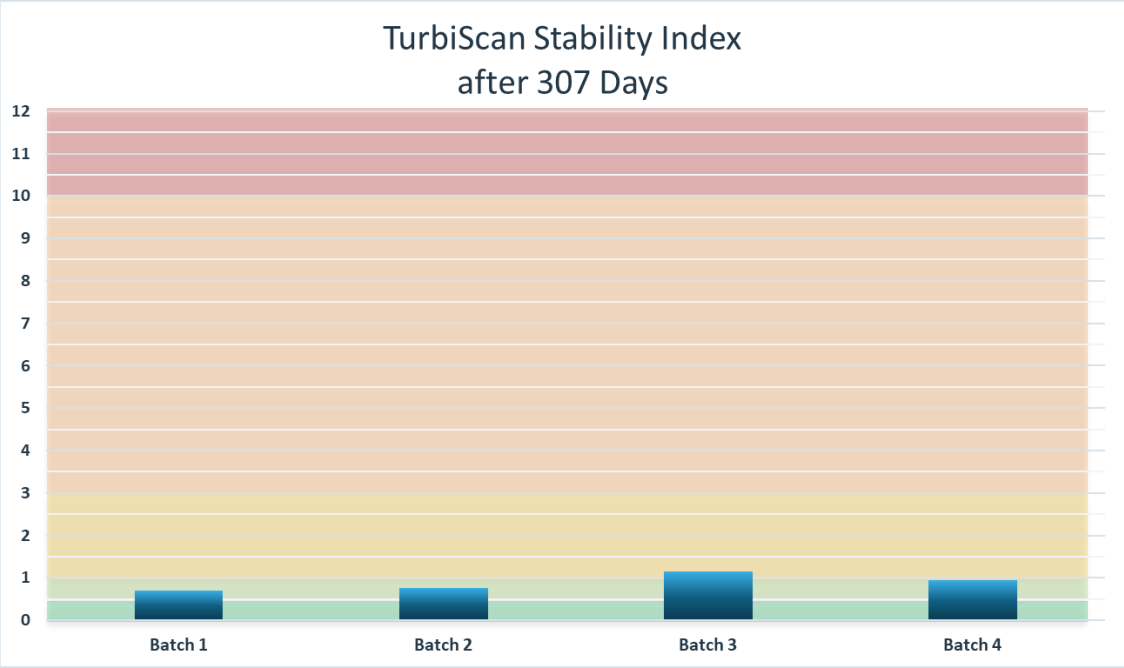
Water Based Dispersion – Stability Testing

- Static multiple light scattering was used to monitor stability of the aqueous GNP dispersions
- Degree of aggregation, agglomeration, sedimentation or phase separation is detected by changes in transmission and backscattering when light is transmitted through the sample
- The Turbiscan Stability Index (TSI) is a Turbiscan® specific parameter developed for formulators to compare and characterize the physical stability of dispersions
- The TSI calculation is based on an integrated algorithm that sums up the evolution of T or BS light. Ultimately, TSI corresponds to a cumulative sum of all the Backscattering or Transmission variation of the entire sample.



Turbiscan Stability Index

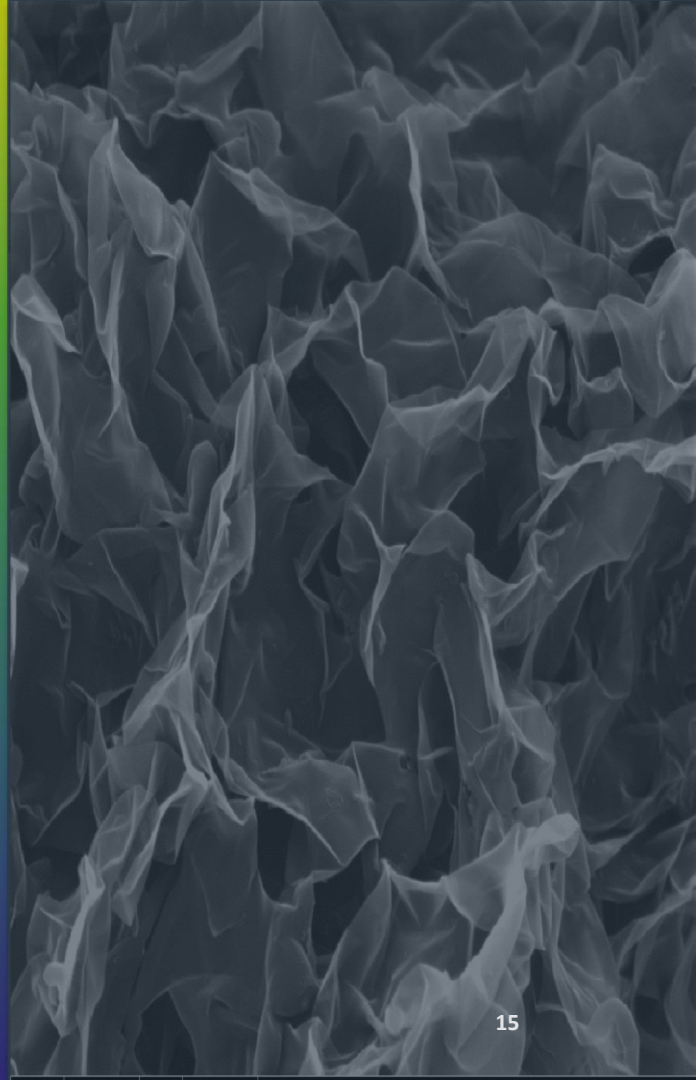
Water Based Dispersion – Stability Testing



- Stored at ambient conditions for 307 days, all samples showed **no visible signs of destabilization**.
- The Turbiscan categorized 3 batches an “A” Rating with one just falling in to the “B” Rating zone
- Rating “A” and “B” are both categorized as **Visually Stable Passes**

Water - Based Dispersion

Experimental



Formulations

		Weight%		
	Raw Material	**Control System**	**5% GNP Dispersion System**	**10% GNP Dispersion System**
	Part A: Epoxy Base			
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%

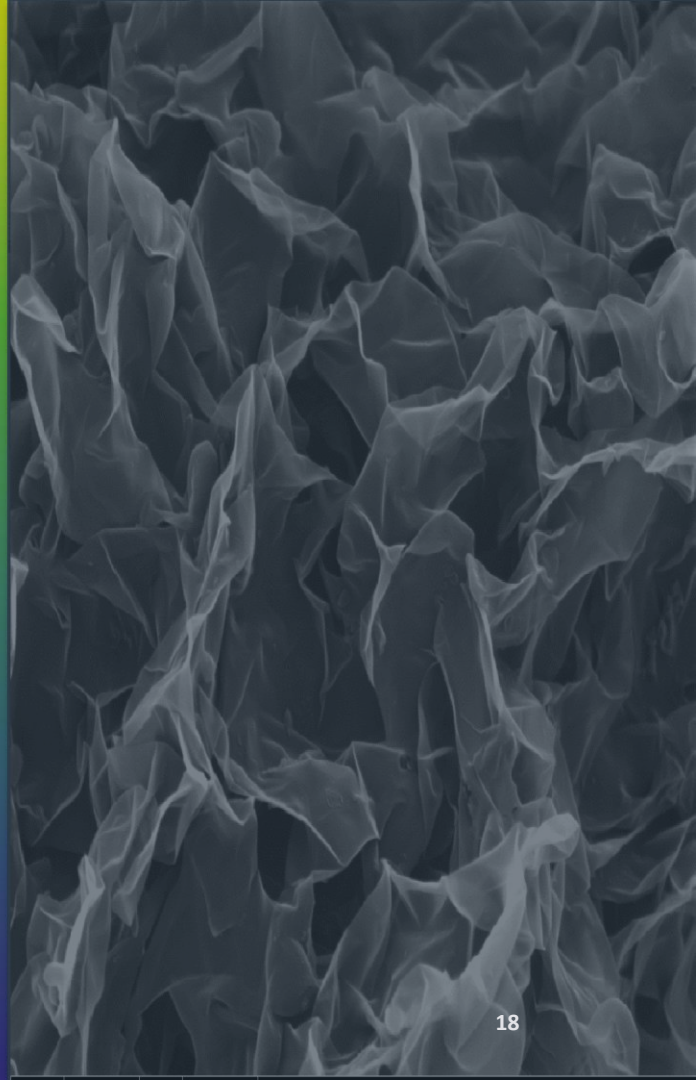
Test Program

- 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 performance benefits of the graphene enhanced water based coatings for use as **anticorrosive primers**:
  - Neutral salt spray – ISO 9227
  - 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 (300µm)
Coating Thickness	DFT 80 – 100 µm
Curing	7 Days at Room Temperature @ 25°C

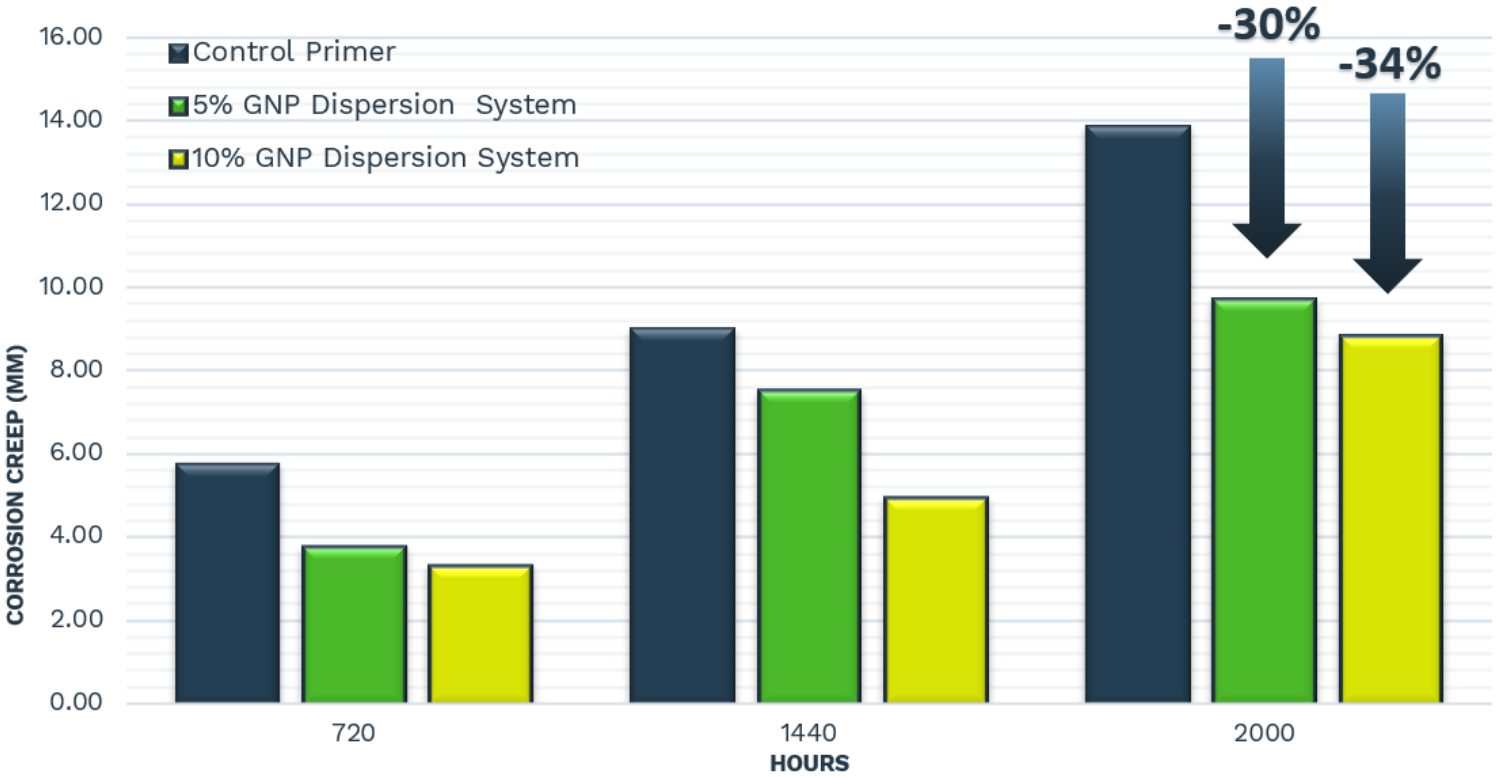
Results

Neutral Salt Spray & Electrochemical Impedance Spectroscopy



Neutral Salt Spray – ISO 9227

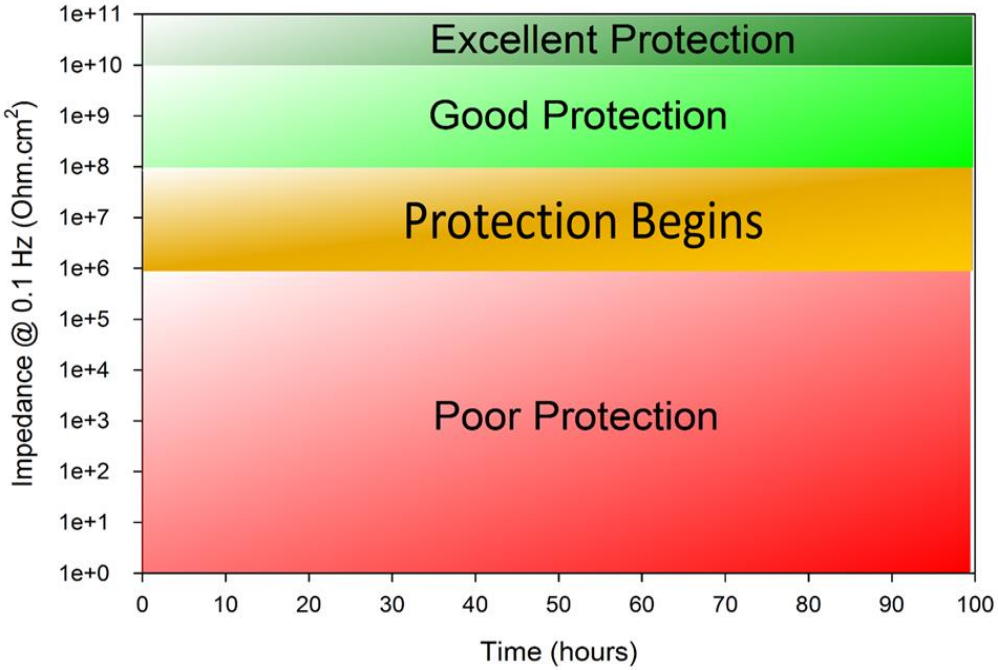
2000hours- Creep Assessment



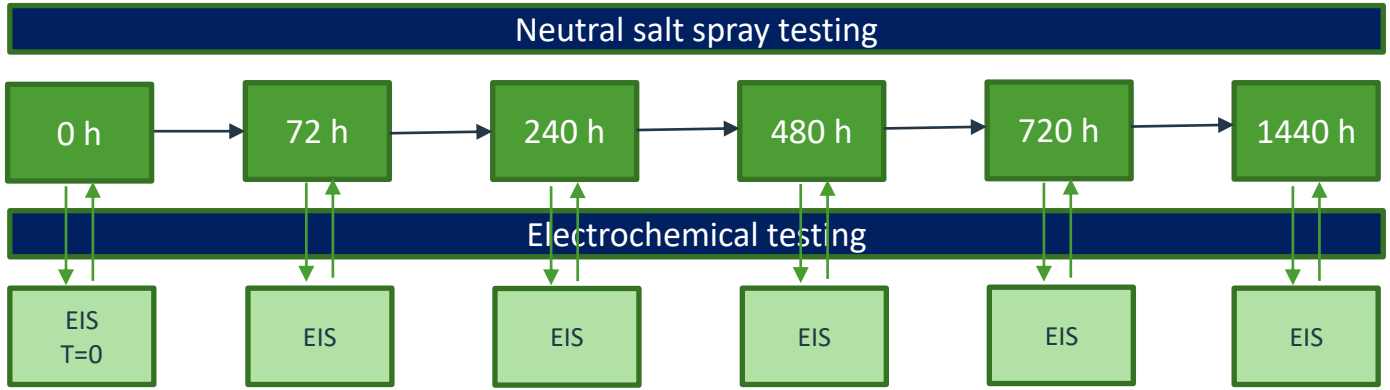
Electrochemical Testing

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 every 10 days for subsequent testing



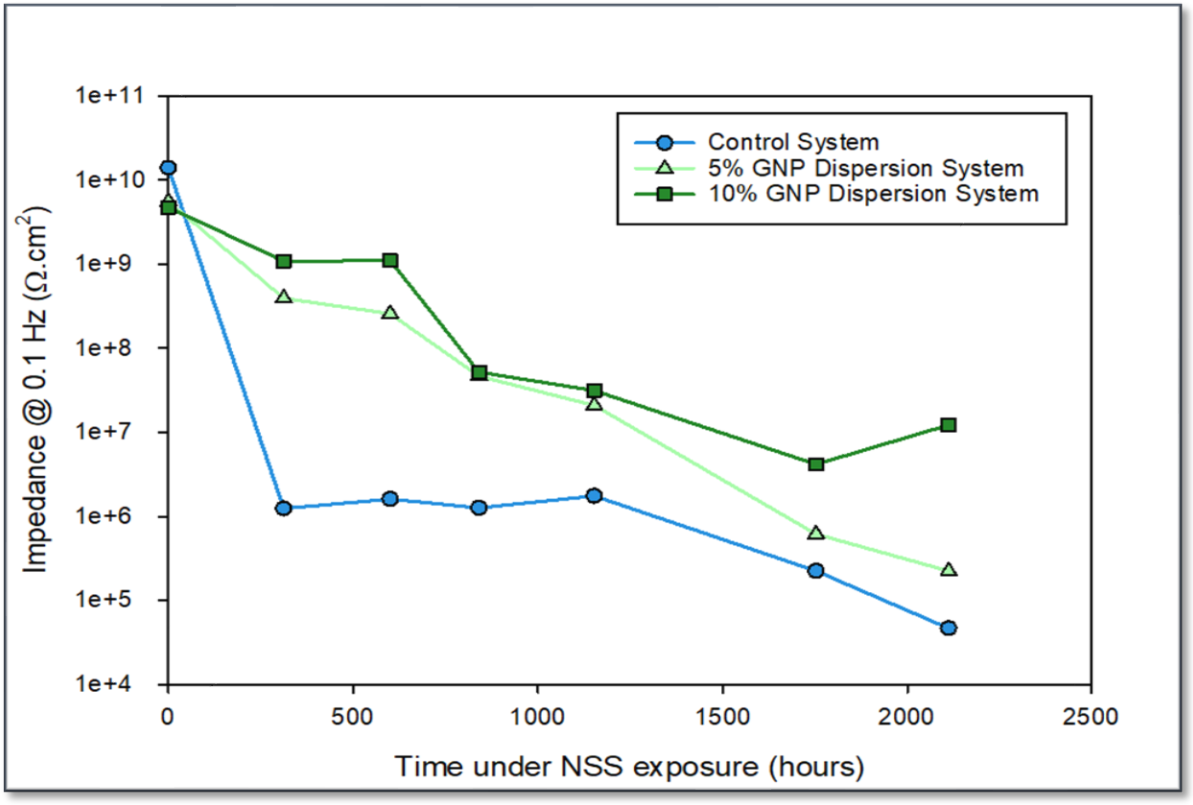
Combined Testing



Dual testing approach

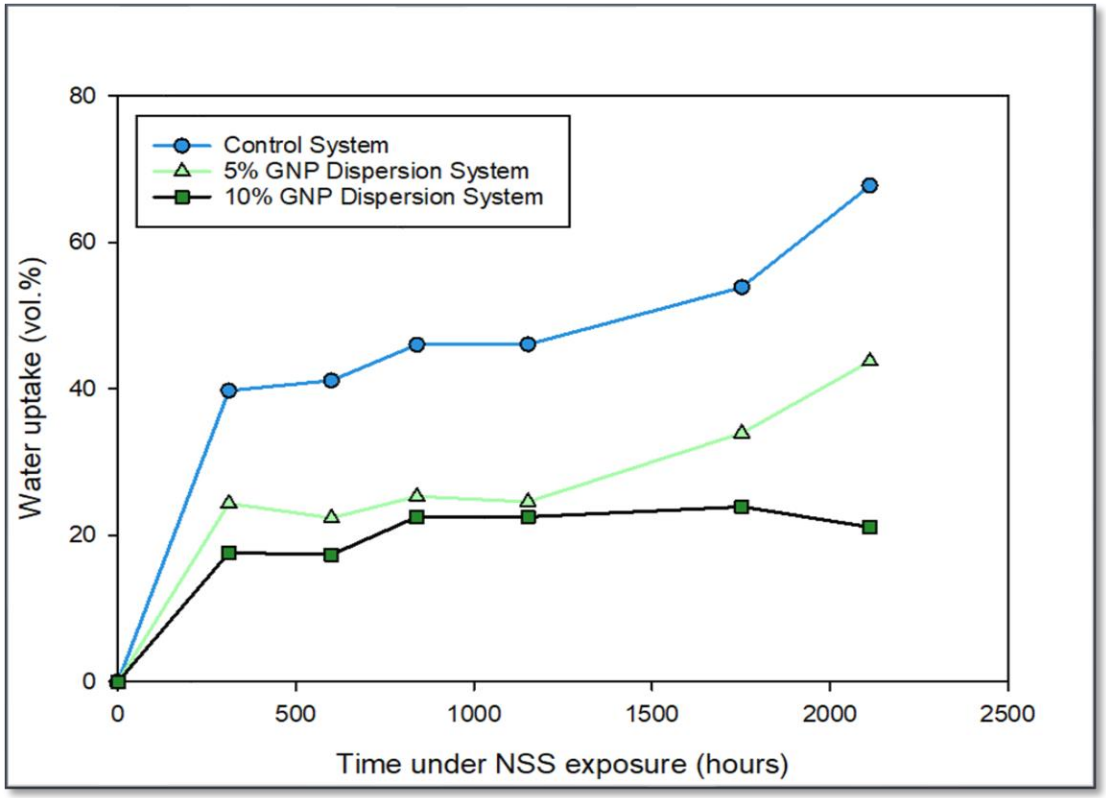
- Combined tests are complimentary to each other since EIS can determine relatively small changes within the coating during the NSS testing, this can give an indication of performance prior to any visible coating changes seen from examination of the panels
- The test conditions of NSS are more realistic 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 Testing – Impedance



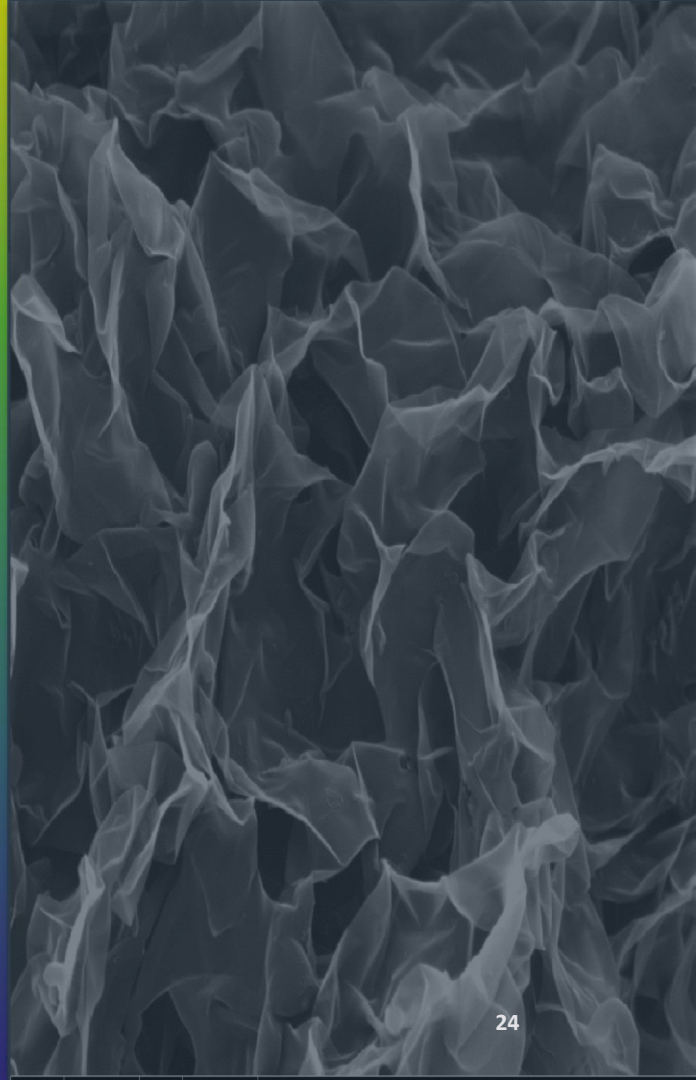
- Both Graphene loaded paints had **higher levels** of impedance compared to the blank control primer
- The **highest impedance** coating was with the **10% GNP dispersion** sample = 0.05% GNP solids
- This suggests both samples possess **better barrier** properties over the control sample.

EIS – Water Uptake



- Over the duration of the combined EIS/NSS test, the blank control showed a **very high water uptake**, at the end of the testing cycle having just under a **70%** by volume water uptake
- In contrast, both of the graphene enhanced coatings showed **significantly less** water uptake
- With the higher loading showing a water uptake of just under **20%**
- This further re-enforces the theory of a barrier mechanism

Summary and Conclusions



Summary

High Quality Dispersions

- Despite the significant challenges in the development of graphene nanoplatelets dispersion, AGM have demonstrated that their proprietary process delivers **stable**, **easy to incorporate**, **safe** dispersions with reliable **batch to batch reproducibility**

Water based Anti Corrosion Performance

- The addition of AGM's water based dispersion has shown to deliver improvements in anticorrosion performance through

i. Reduction in blistering and over **30%** reduction in creep on NSS testing

ii. Significantly **higher impedance** values over 2000 hours of testing

iii. **Substantial** reduction in water uptake with graphene enhanced coatings

Conclusions

- Dispersions of graphene nanoplatelets offer **easy to use solutions** that enable formulators a simple way to **innovate with graphene** and benefit from its **value adding properties**

- Graphene nanoplatelet dispersions offer coatings formulators a new **toolbox technology**, giving to opportunity to offer their customers a new **innovative solution** to **combat corrosion**

- With the addition of AGM's stable dispersions, **significant improvements** in the performance of a water-based anti-corrosion coating can be achieved, providing the potential for **extension of coating life** adding real value to the market

- As the coatings industry moves towards **sustainable** and **environmentally beneficial** technologies, graphene is a **viable alternative** to traditional heavy metal based anti-corrosion additives

Find out more….?

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