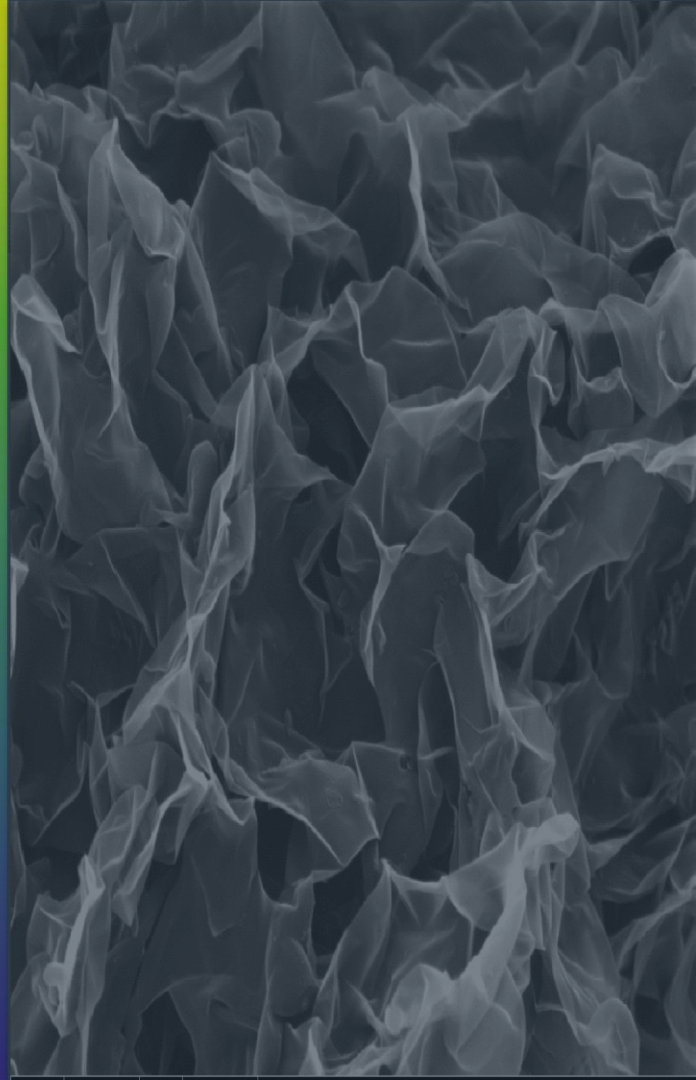**APPLIED GRAPHENE MATERIALS**
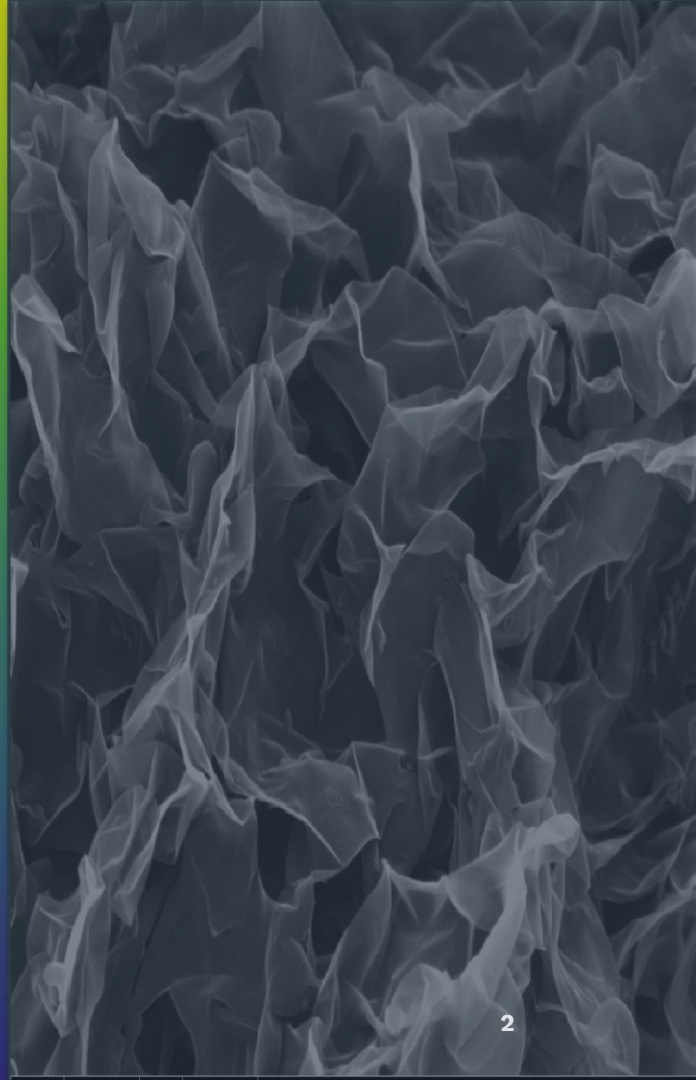
Graphene: Challenging the Boundaries of Corrosion Prevention

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Introduction

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- ⬡ Graphene as a 2D nanomaterial has been extensively researched as a new additive to improve barrier performance, reduce corrosion and extend service life.

- ⬡ The two-dimensional structure of graphene nanoplatelets (GNPs) with high surface area and high aspect ratio makes them particularly suitable for use as multi-functional additives in paints and coatings.

- ⬡ The proposed mechanism by which graphene delivers anticorrosion performance is a combination of physicochemical processes restricting uptake of water (combined with oxygen and salt) and electrochemical activity.

- ⬡ There is also evidence in literature of graphene behaving as a free radical scavenger, which may in turn improve the durability of coatings.

Previous Work – Performance enhancements of Coatings for C4/C5 Environments

- In previous work, the authors demonstrated improvements in anticorrosion performance of C4/C5 primers, with the inclusion of graphene.

- The improvements were demonstrated by high impedance values, lower water uptake, as well as a reduction in creep (on neutral salt spray).

- The graphene enhanced epoxy paints were then incorporated into a 3 coat system as a tiecoat. Systems were exposed to NSS and impedance for 1440 hours.

- Significant improvements in impedance were noted, as well as significant reductions in water uptake.
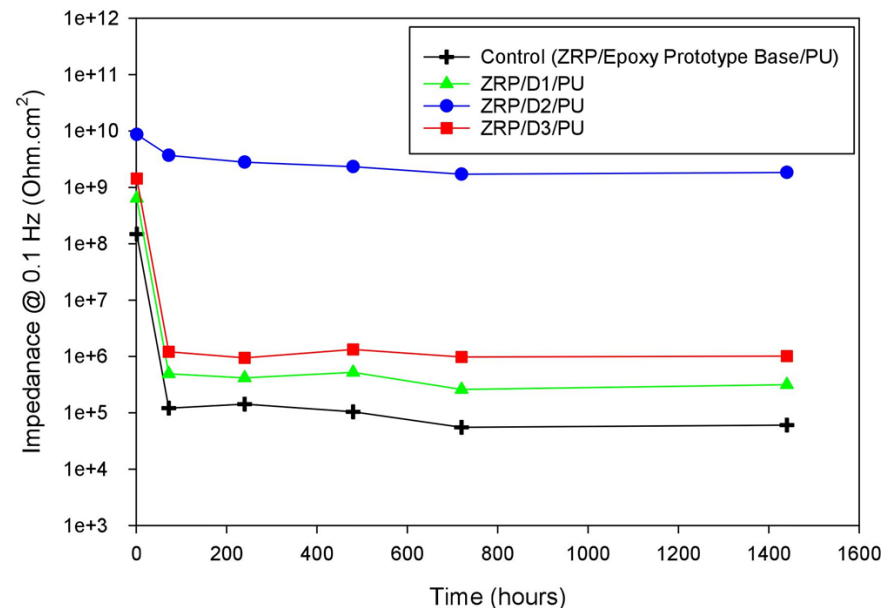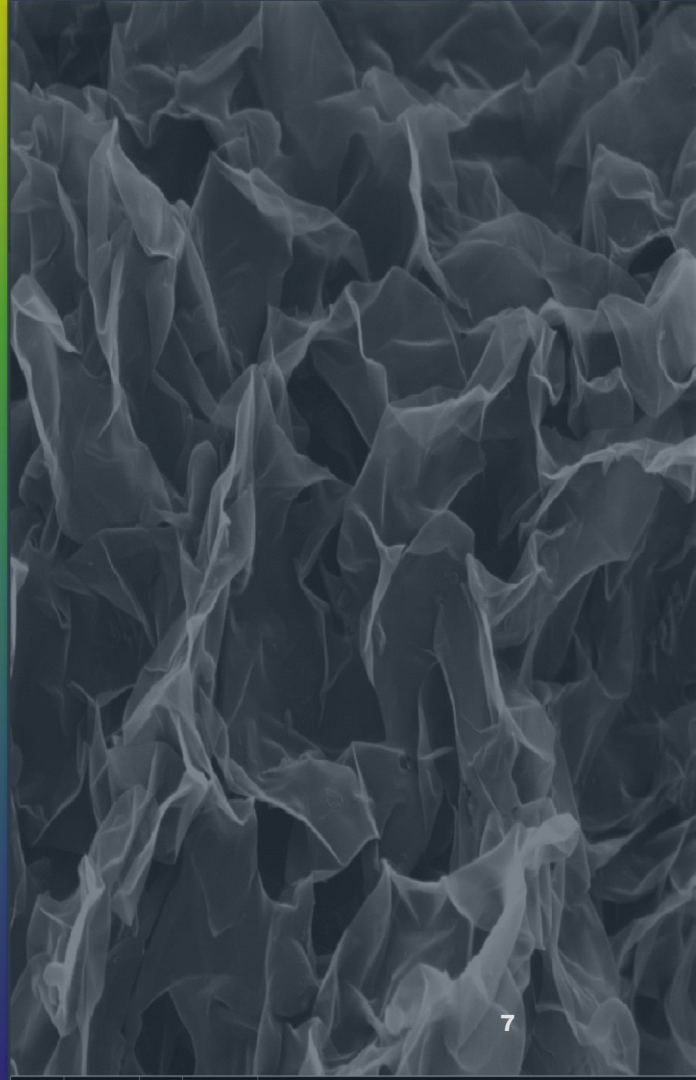
The Challenge

- Corrosion remains a key challenge for the protection and maintenance of infrastructure, with the result of failure having the potential for significant impact both financially and on human lives.

- The CX environment (as defined in ISO 12944) is classified as the most extreme type of environment and may include offshore, industrial, sub-tropical and tropical areas with very high humidity, high salinity and sometimes full immersion.

- Having previously demonstrated significant uplifts in anticorrosive performance in solvent and water-based coatings for medium challenge environments (C3-C5), through the use of graphene nanoplatelets (GNPs), the authors present on an extension of the use of graphene nanoplatelets into CX applications.

Objectives

○ For this work, the authors report on an extension of previous work, investigating performance enhancements under CX (harshest corrosivity) environments, as defined in ISO12944 Part 9, with two main objectives:

1. Investigate whether inclusion of graphene improves anticorrosive performance of CX primers.

2. Use accelerated EIS techniques to measure performance and predict long term performance of CX coatings.

Experimental

Graphene Nanoplatelet Dispersions

- Dispersion and incorporation of graphene nanoplatelets **can be** challenging as carbon based pigments/materials have an affinity for each other and will tend to **flocculate**, **agglomerate** and **aggregate.**

- Furthermore, GNPs, when unstabilized, have a tendency to **"re-stack"** with the nanoplatelets agglomerating across the platelet lateral surfaces, resulting in an **increase in the thickness** of the GNP sheets

- In order to achieve optimal incorporation of graphene into paints and coatings, GNPs are pre-dispersed into a suitable host matrix, using a process that is designed to achieve the most stable dispersions.

Graphene Dispersions

○ For this work, two GNP types were used, synthetic graphene (GNP A) and natural exfoliated graphene (GNP B)

○ GNP A and GNP B were incorporated into a liquid epoxy resin, known to be compatible with the prototype CX formulation.

○ Owing to the different properties of GNP A and GNP B, the masterbatch graphene dispersions were prepared at different loadings.

	Graphene Dispersion A	Graphene Dispersion B
Dispersion Matrix	Liquid epoxy resin (EEW = 185-192)	Liquid epoxy resin (EEW = 185-192)
Graphene Type	Synthetic graphene – GNP A	Natural exfoliated graphene – GNP B
Graphene Concentration	1%	10%
Recommended use level (GNP)	0.025 to 0.1%	0.05 to 1%

Paint Formulation

- An epoxy prototype base was formulated to be representative of a typical **CX epoxy primer, using a blend of semi-solid and liquid epoxy resin and aluminium flake (commonly used as an anticorrosive pigment for CX primers).**

- For the graphene enhanced CX primers, the GNPs were added through addition of either Graphene Dispersion A or Graphene Dispersion B, at the let down stage.

- In order to achieve a meaningful comparison, the systems were tested against two commercially available standard formulations. Key characteristics of these systems are summarised in the table below:

System Tested	Chemistry	Volume Solids (%)	VOC (g/l)
Commercial CX Primer 1	Epoxy high volume solids aluminum/fibre pigmentation	79	178
Commercial CX Primer 2	Aluminum- pigmented epoxy	60	386

Formulations

| Part A	Control	0.025% GNP A	0.05% GNP A	0.05% A-GNP B	0.5% A-GNP B
Semi-solid epoxy resin (80% solution in xylene)	18.58%	19.39%	20.28%	18.65%	19.25%
Medium viscosity epoxy resin	11.57%	9.59%	7.42%	11.18%	7.49%
Mono-functional epoxy reactive diluent	6.34%	6.62%	6.92%	6.36%	6.57%
Graphene Dispersion A (1% loading of GNP A)	-	**2.52%**	**5.27%**	-	-
Graphene Dispersion B (10% loading of GNP B)	-	-	-	**0.48%**	**5%**
Xylene	8.78%	9.17%	9.59%	8.81%	9.10%
Butanol	3.76%	3.93%	4.11%	3.78%	3.90%
Epoxy functional silane adhesion promoter	0.97%	1.01%	1.05%	0.97%	1.00%
Polyamide Heat Activated Thixotrope	1.25%	1.31%	1.37%	1.26%	1.30%
Talc	21.18%	17.70%	13.90%	20.86%	17.83%
Yellow iron oxide	3.86%	4.03%	4.21%	3.87%	4.00%
Red iron oxide	0.48%	0.50%	0.53%	0.48%	0.50%
Aluminium flake (paste in mineral spirits)	4.19%	4.37%	4.57%	4.20%	4.34%
Part B					
Solvented Phenalkamine hardener	14.63%	15.27%	15.97%	14.68%	15.16%
Low viscosity Phenalkamine hardener	3.38%	3.53%	3.69%	3.39%	3.50%
Tris-(dimethylaminomethyl) phenol	1.01%	1.06%	1.11%	1.02%	1.05%
Total	100.00%	100.00%	100.00%	100.00%	100.00%

All systems were formulated to a PVC of 20%, with a resultant volume solids of 68% and a VOC of 276g/l.

Test Program

Panel Preparation

- Cold rolled steel panels (of dimensions 150 x 100 x 2mm) were degreased and blasted to SA 2.5

- Coatings were applied using conventional spray application methods.

- All panels were cured for 7 days under ambient lab conditions.

- Testing was carried out at low and high dry film thicknesses (DFT).

  - Low DFT systems were applied at 150 microns, while the high DFT systems were applied at 350 microns.

- Testing was carried out on one intact panel and one scribed panel.

PERFORMANCE TESTING - REAP

- The rapid electrochemical assessment of paint (REAP) method is a test method designed to determine the long-term performance of coatings on metallic substrates using short term tests.

- The test method was first described in detail in a journal article published by Kendig et. Al. in 1996, who studied the correlation of several electrochemically-measured factors to the time to failure.

- The 3 key factors which feed into the REAP method are water uptake, corrosion resistance and cathodic disbondment. From these values, a relative time to failure can be calculated.

- While the standard test duration is 24 hours, for this test program, testing was carried out for 504 hours with high DFT testing being carried out at 1008 hours.

Water Uptake

Relative Time to Failure

Cathodic Disbondment

Corrosion Resistance (Rcor)
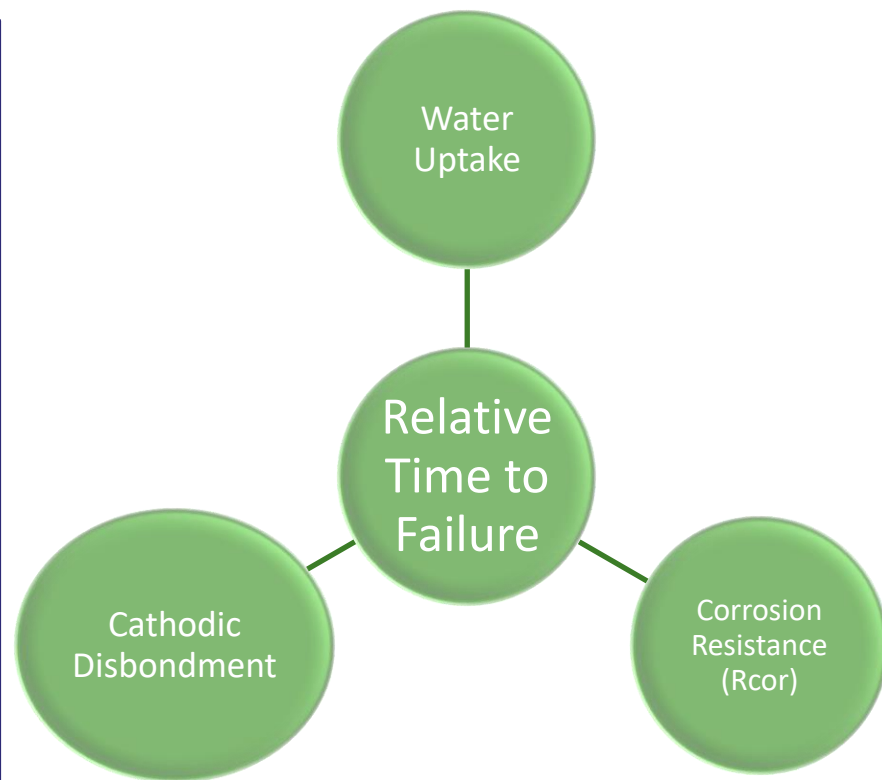
Water Uptake

- Water uptake was determined by soaking low DFT panels for 3 weeks (504 hours) and high DFT panels for 6 weeks (1008 hours).

- Coating capacitance was determined at the start and at the end of the test.

- The two coating capacitance values were then used to calculate water uptake for each coating.

- Influx of water into the coating leads to an increase in the volume fraction of water and so an increase in overall permittivity.

Corrosion Resistance (RCor)

- Rcor or corrosion resistance is an interfacial parameter which governs electron transfer within the redox reactions which drive corrosion.

- In order for this parameter to exist, electrolyte must exist at the metal-coating interface; a breach of the coating is therefore required.

- On the standard REAP test, Rcor is measured after 24 hours of exposure to the electrolyte.

- As with the water uptake testing, duration of testing was adjusted on our testing, with Rcor being tested after 3 weeks (504 hours) for low DFT primers and 6 weeks for the high DFT systems.

Cathodic Disbondment

○ Unlike water uptake and RCor, Cathodic Disbondment was tested on scribed samples. This is because disbondment tends to initiate at the point of damage.

○ Under the standard REAP test, samples are subjected to 24 hours of cathodic disbondment, under a cathodic potential of -1.05V

○ Disbondment length (creep) is then measured and used to calculate the disbondment rate.

Electrochemical Testing

Equipment setup

- Measurements recorded using a potentiostat in conjunction with a multiplexer
- A conventional three electrode system was used
  - Coated metal substrate as the working electrode and a graphite rod served as the counter electrode
- The test area of the working electrode was 14.6 cm^2 and run using a 0.5 M NaCl electrolyte.
- For EIS experiments, 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
- For cathodic disbondment, a potential of -1.05 V (Vs SCE) was applied, potentiostatically
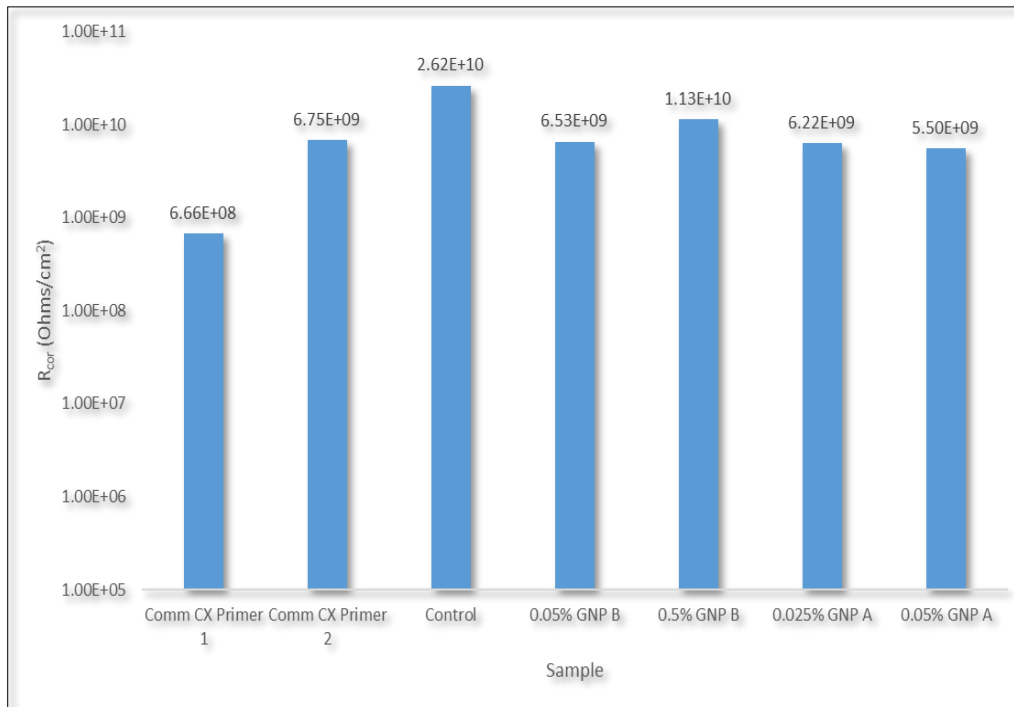
# Results
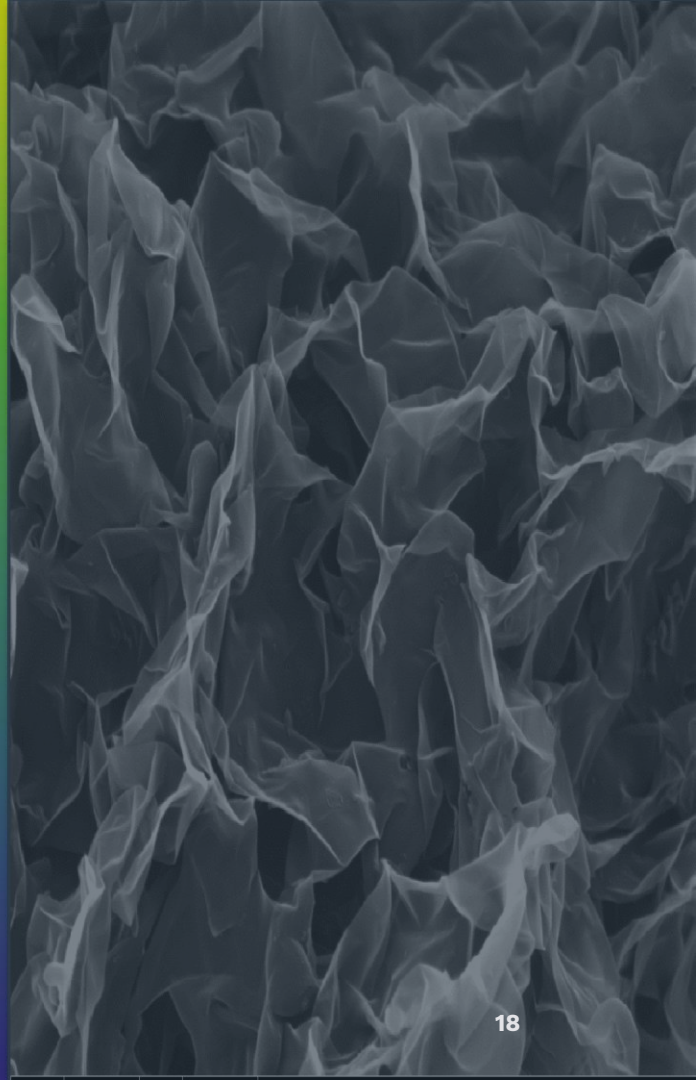
Low DFT - Water Uptake
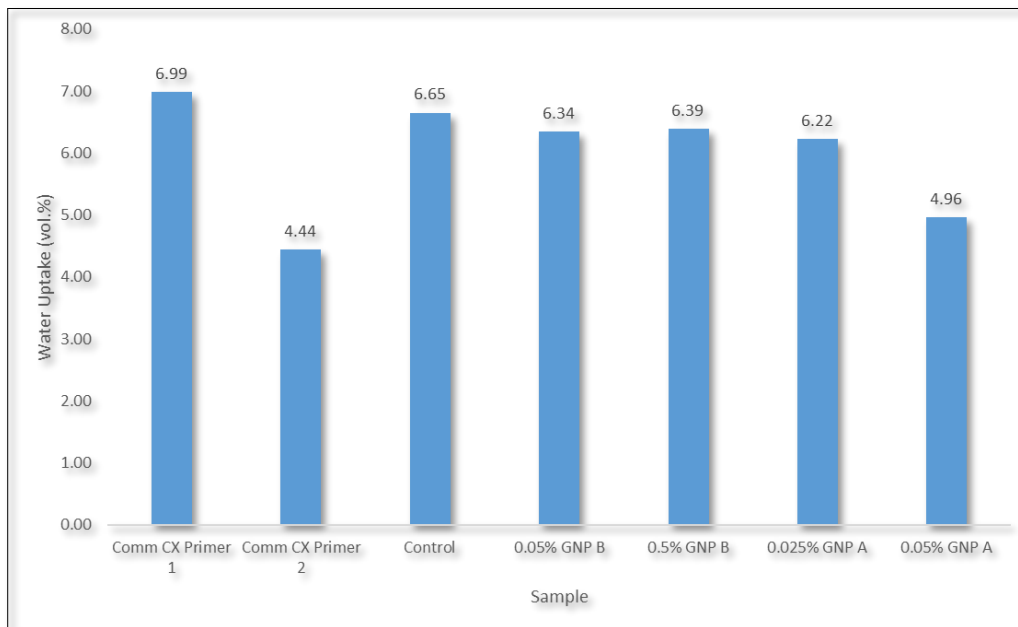
- Water uptake was determined after samples were exposed to the NaCl electrolyte solution for 3 weeks.
- 0.05% GNP A showed a meaningful (25%) reduction in water uptake compared to the graphene-free control.
- Overall, Commercial Primer 2 gave the lowest water uptake values.
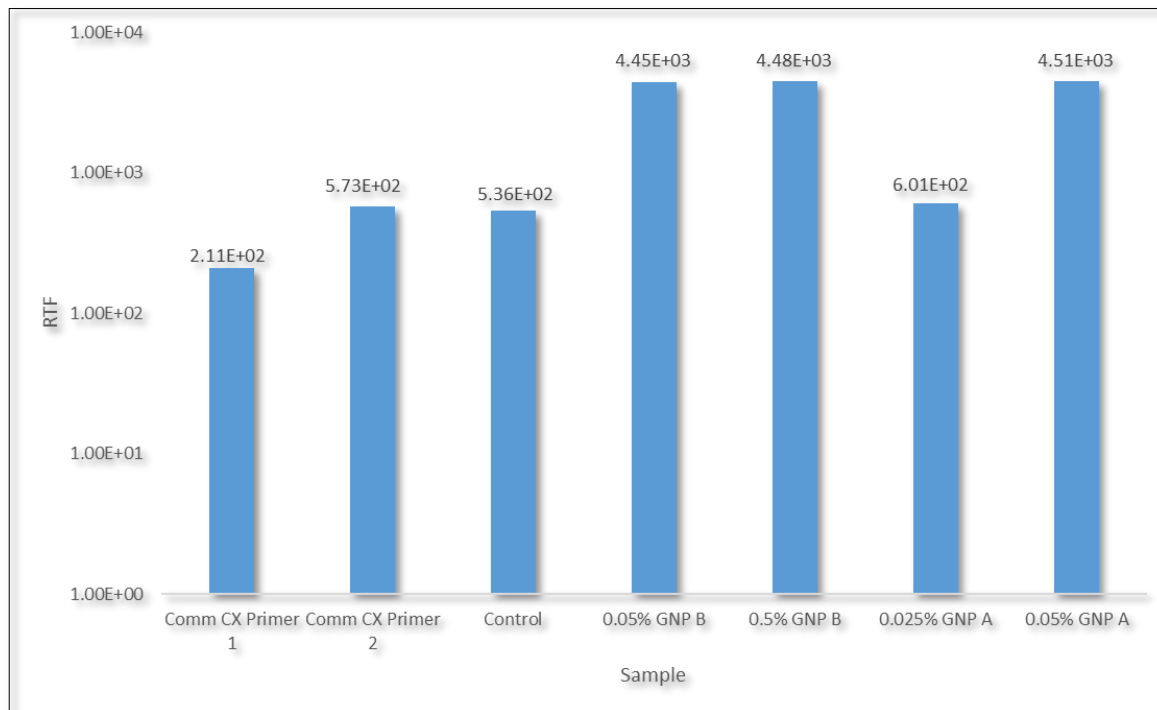
Low DFT R$_{Cor}$ (Corrosion Resistance)

- The majority of the values are very close to each other suggesting an equivalent level of performance for these coatings.

- Rcor value for the Commercial CX Primer 1 sample is close to two orders of magnitude lower than the GNP-free Control sample, suggesting a higher corrosion rate and lower performance for this sample

Low DFT Mean Disbondment Rate
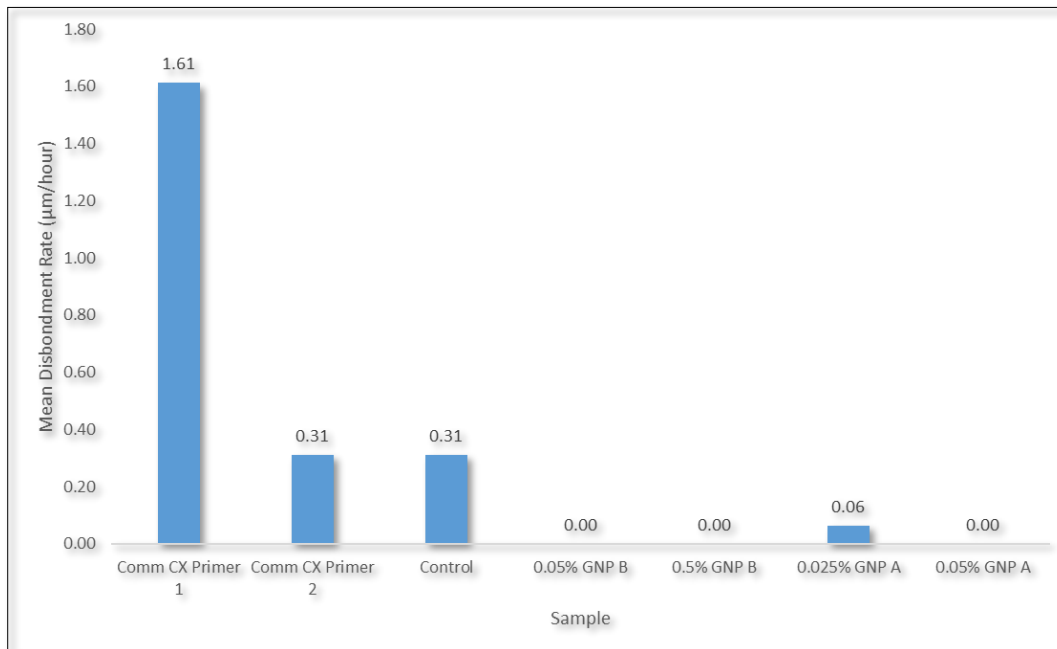
- Both samples of GNP B, showed no disbondment
- Low loading of GNP A showed minimal disbondment, while the high loading showed no disbondment.
- In all cases, the graphene modified systems demonstrated a significant reduction compared to the control and both commercial standards.

Low DFT Relative Time to Failure

- Using the three REAP parameters of water uptake, corrosion resistance and cathodic disbondment, it was then possible to derive the relative time to failure (RTF).

- At this DFT, the two samples of GNP B and the higher loading of GNP A showed a longer relative time to failure compared to the control and commercial standards.

- Addition of graphene may extend durability of CX coatings.

High DFT – Water Uptake
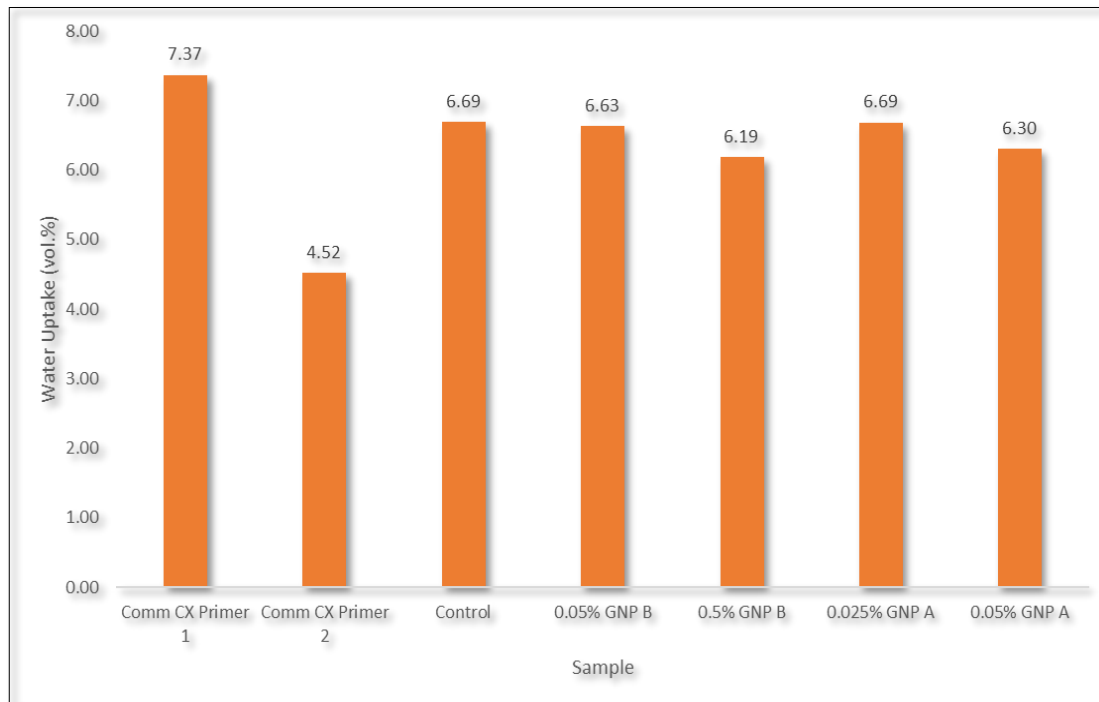
- Overall, it was found that the Commercial CX Primer 1 samples gave the highest water uptake, while Commercial Primer CX 2 samples gave the lowest value for water uptake.
- The graphene-modified samples showed little difference in water uptake from the control sample.
- It is possible that the addition of graphene to these already very highly pigmented systems makes little difference to water uptake, although it does not appear to promote it.

High DFT – Mean Disbondment Rate
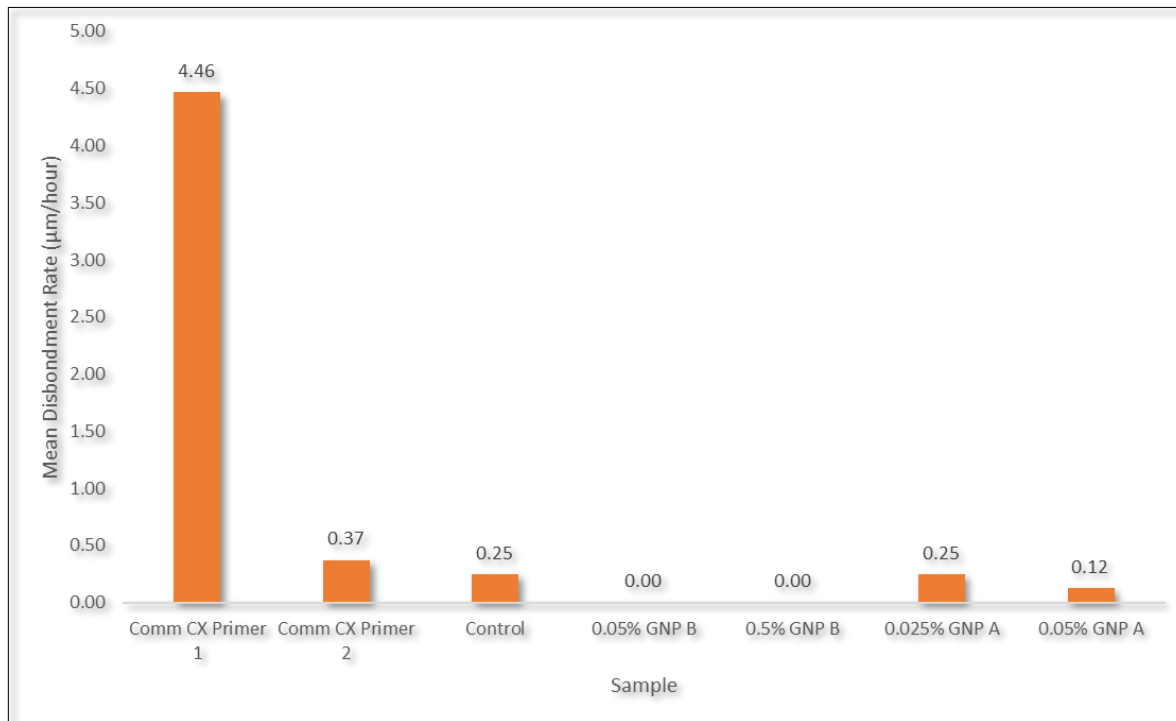
- Both of the GNP B samples (0.05 and 0.5 wt.% GNP) showed no measurable disbondment creep, suggesting a superior performance under cathodic conditions.
- Higher loading of GNP A (0.05%), also showed a reduction in rate of disbondment.

High DFT REAP

- In order to calculate relative time to failure, three REAP parameters are needed, namely water uptake, Rcor and disbondment rate. However, for the high DFT samples (~350um), it was not possible to measure Rcor, due to a lack of electrolyte at the interface.

- However, given the similar trend in mean disbondment rate, it would be reasonable to expect that the two GNP B coatings, as well as the higher loading of GNP A, would potentially demonstrate a longer relative time to failure.

Discussion and Summary

Summary

- A modified version of the REAP method is presented, adapted to take account of coatings designed for CX environments, by varying coating film thickness and increasing test duration.

- Overall, it can be inferred from the testing on low DFT coatings that inclusion of GNP B at low or high loadings or the higher loading of GNP A, could extend a coatings relative time to failure; suggesting that graphene, at the right loadings, may extend the durability of a primer under CX conditions.

- At higher DFTs, and a longer test period of 6 weeks, it was found that, for all samples, R_{cor} could not be determined, owing to the fact that there was no electrolyte breakthrough at the coating-substrate interface. This is not surprising as CX coatings at these high DFTs are designed to last up to 25 years under the harshest corrosivity environments.

Discussion

Through REAP testing it has been observed that graphene, introduced into coatings, appears to improve cathodic delamination performance when the coating is placed under a cathodic environment. This may be a result of either:

1. Improved barrier properties. Graphene is widely reported to improve barrier properties of coatings. However, minimal changes in water uptake were recorded in this work, suggesting another mechanism for the improvements shown.

2. Free radical scavenging. Work carried out by Kolanthai et. al on graphene enhanced polymer composites, suggests that graphene can behave as a free radical scavenger. It has also been demonstrated that free radical scavengers can reduce coating delamination that is caused by cathodic disbondment. It is possible, therefore, that the graphene materials are reducing cathodic disbondment through a similar free radical scavenging mechanism.

Further work would be required to verify the mechanism at play.

Further Work

- Further work is currently underway to carry out testing defined for CX coatings in ISO12944. This work is expected to be finalised end of September 2021.

  - Cathodic disbondment testing (ISO 15711)

  - Artificial Seawater Immersion testing (ISO2812-2)

  - Cyclic ageing tests (as defined in ISO 12944 Part 9).

- Review correlation of the results of the REAP testing with the widely accepted standard test methods.

- Further work to verify whether the improvements seen in cathodic disbondment are due to free radical scavenging and or the barrier properties of graphene.

APPLIED GRAPHENE MATERIALS

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