Physical Impacts of Graphene on Polymers and Corresponding Impact on Protective Coating Performance Under Corrosive Conditions

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ABSTRACT

High solids epoxy coatings remain a key component of coating systems used for the prevention of corrosion in steel structures, particularly for service in highly corrosive, atmospheric exposed environments. These environments include offshore and onshore structures in oil, gas, petrochemical, chemical and energy plants.

Over >6 years we have been able to identify the key characteristics that support specific grades of graphene being optimal for enhancing the performance of epoxy based protective coatings. Effectively dispersed graphene of the correct physical and chemical composition has been shown to materially improve the physical properties of high solids epoxy coating formulations. Data has been collected from numerous studies carried out to global standards including corrosion and crack resistance to support this thesis, along with preliminary results from field testing.

Mechanical performance improvements seen in graphene enhanced epoxy coatings have also been seen in solid polymers of various kinds. The results provide strong evidence that graphene acts to support the polymer matrix and behaves as a shock absorber when the polymer / protective coating becomes "stressed" while in service.

The clear performance benefits demonstrated in these studies offers high potential for improved asset protection and service life through the use of graphene enhanced epoxy coatings on critical steel infrastructure. Significant cost and CO_2 emissions savings can be delivered for asset owners through reduced maintenance and downtime over the life of the steel structure.

Key words: Epoxy Coatings, Corrosion Protection, Extended Service Life, Mechanical Properties, Graphene.

INTRODUCTION

Protection of steel infrastructure is essential for asset performance and safety, especially in highly corrosive environments. Epoxy coatings are the most common type of protective coating used on steel, representing almost 40% of the market. Specifically, two component epoxy polymer systems have been used as the basis for high performance protective coating systems since the 1950's. Numerous resin types and ambient condition curing agents are available today which allow great flexibility in the formulation of epoxy coating products. This has led to their use in a wide range of applications ranging from simple anticorrosive systems to high performance heat and chemical resistant coatings and linings. Over the years, a large body of knowledge has been accumulated regarding the performance properties and limitations of epoxy coating systems.

Properties of adhesion, film toughness and general chemical resistance are very important in achieving the required durability in epoxy coatings. Brittleness and cracking of epoxy coatings and linings in service is a known issue. Current formulation techniques such as reduced crosslinking or introduction of diluents to reduce film brittleness can impact on the overall chemistry of the coating film leading to compromised coating durability and performance. Given the mission critical nature of much of the infrastructure that epoxy coatings protect, formulation changes require significant evaluation before adoption into commercial products.

Graphene is a material which is defined as a single (2D) layer of carbon atoms bonded in an indefinite lattice structure. Since the Nobel-prize-winning discovery of graphene in 2004[1], a significant amount of effort and activity has gone into incorporating graphene within industrial materials to impart some of graphene's exceptional properties including strength, conductivity and flexibility. Despite the significant potential of graphene to improve the performance of protective coatings, widespread commercial adoption has not yet occurred. It follows that there is very limited commercially applicable data around graphene and its impact on protective coatings.

We have shown the ability of low dosages of graphene with the right physical and chemical composition to improve the mechanical properties of an epoxy coating film via physical reinforcement of the polymer system, without any chemical changes. This technology has potential application in any area where the mechanical properties of epoxy resin systems are a factor in performance – other examples being adhesives and composites. It is also likely that this approach can be transferred to other polymeric systems used in industry. In this paper, we examine the influence of carefully selected graphene grades on the performance of a range of epoxy based protective coating systems and suggest a mechanism by which this is occurring.

There are multiple challenges that need to be addressed if the addition of graphene to a polymer system is to be effective. The first is identifying what does improved performance mean. Within epoxy coatings we have targeted an increase in the resiliency and strength of the parent polymer which is evidenced by better anticorrosive performance and enhanced durability delivering a longer effective lifespan in the field.

The second key challenge is identifying a grade of graphene with the correct properties that will impart improved strength and resilience to the polymer matrix. The availability of graphene is widespread with

over 700 grades varying in physical and chemical composition available globally, manufactured by a range of processes at commercial scale[2]. Based on >6 years of experience and evaluation of >100 grades we believe that when graphene functions effectively in an epoxy coating, it impacts the polymer via a supporting mechanism at a primary particle level. The specific graphene grade's unique primary particle structure enables this to occur. Our experience suggests <5% of available graphene grades have the requisite structure and stability to be effective in epoxy coatings.

The third key challenge is one of effective dispersion and long-term stability. Graphene has a natural tendency to reagglomerate into larger 'graphite-like' particles within a liquid medium. If the graphene has agglomerated, its impact as a support to the polymer matrix is nullified. Therefore, the ongoing stable dispersion of graphene over at least two years 'shelf-life' is critical for technical and thus commercial effectivity. Graphene selection and specific dispersion techniques are essential in overcoming this challenge. An example of reagglomerated versus a well dispersed graphene based additive is demonstrated in Figure 1.

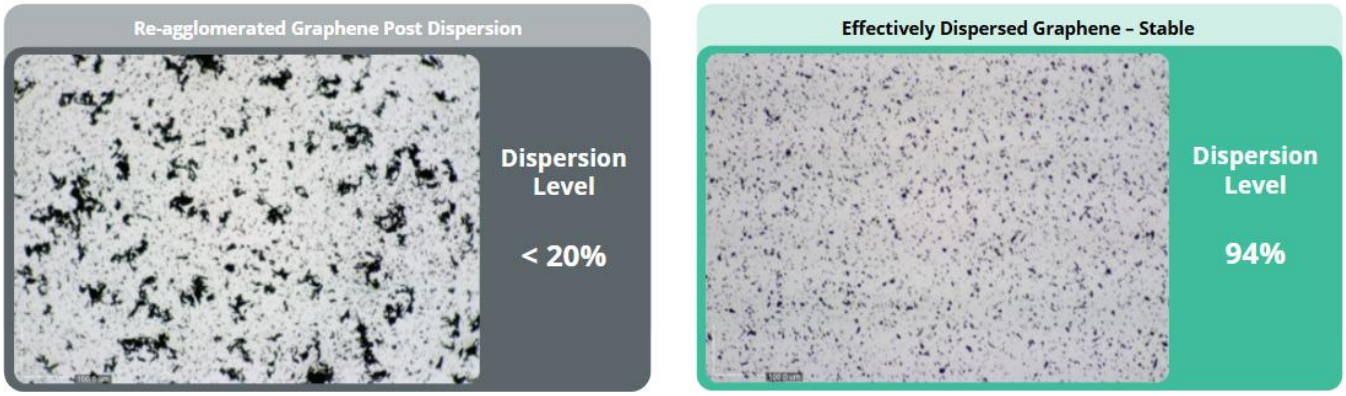


Figure 1. Images taken by a Nikon Eclipse E100 Optical Microscope

The fourth key challenge is one of identifying a method of action for graphene within the polymer system. We spent significant time and effort in understanding how graphene was working to deliver improved anticorrosive performance in epoxy coatings. At a macro level, the proposed, (but not only!), mechanism of graphene in support of an epoxy film is demonstrated in Figure 2. This image was taken at high magnification and displays micro-cracks terminating at graphene particles within the polymer matrix, imparting "stress relief" to the polymer matrix and making the coating more resistant to cracking.

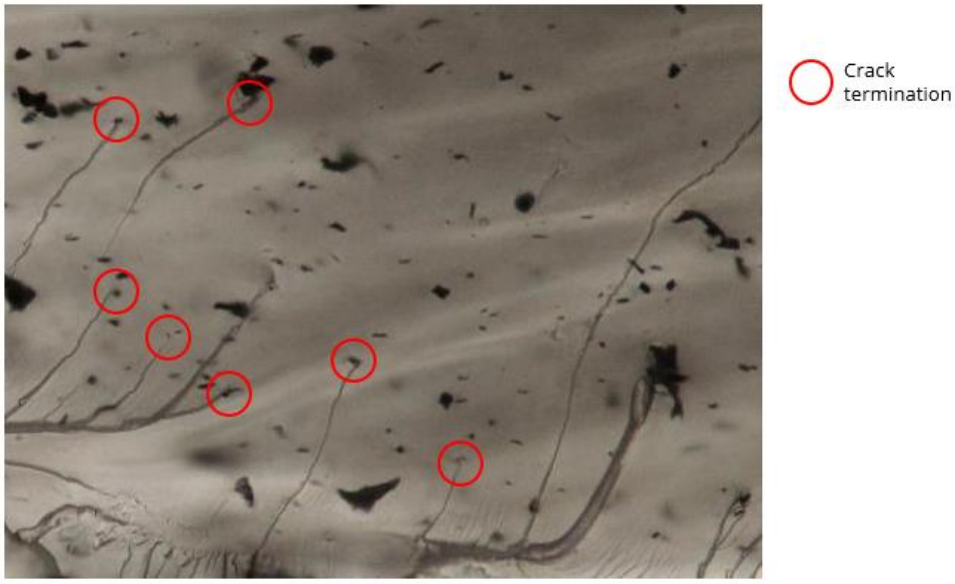


Figure 2. Nikon Eclipse LV100 POL image of graphene dispersed and embedded within an epoxy polymer matrix

The fifth key challenge is one of gaining market acceptance. Given a long history of graphene being tested in polymers and coatings without significant commercial uptake, there is inherent scepticism across the coatings industry. To overcome this 'soft' barrier, it has been critical to have a multi-pronged approach targeting both coatings manufacturers and large asset owners. This approach is considered to be unique for an additive supplier within the protective coatings industry.

1. Build trust through proven results in customers' own language
Over >6 years of technical evaluation, we've gathered knowledge and data. We communicate these findings in the coatings customer's preferred terminology to make the value easily understandable.

2. Address technical skepticism with education and transparent communication
We inform and reassure customers about the science, safety, and performance of graphene enhanced protective coatings through open dialogue and supporting evidence.

3. Collaborate directly with downstream users and asset owners
We work closely with global end users of protective coatings—such as oil and gas companies (e.g., Aramco), mining companies (e.g., BHP) and Governments—to integrate graphene-enhanced coatings into specifications through field and lab-based testing.

The following experimental evidence will support our thesis that correctly dispersed, dosed and graded graphene incorporation can lead to substantial improvements in the mechanical and anticorrosive properties of high solids epoxy coatings. This is demonstrated through quantitative measurements of scribe creep utilising either Electrochemical Impedance Spectroscopy (EIS) or ISO12944, crack resistance as measured by a variation of the TM0404 - Thermal Cycling Resistance Test methodology, and increases in strength as measured by elastic modulus.

EXPERIMENTAL PROCEDURE

This project was initiated as an examination of the potential for graphene to improve the anticorrosive performance of epoxy coatings. In particular, we examined the type of coatings used in marine and protective coatings industries as non-inhibitive anticorrosives for immersed and atmospheric service over

steel substrates. The coating systems used in these areas range from 75 microns single coat systems to multicoat systems of 500 microns or more.

Initial screening work was aimed at selecting graphene grades suitable for this purpose from a wide range of experimental and commercially available materials. Later work focused on optimization of graphene dosage levels in a range of commercially available epoxy coating products specifically targeting grades considered “fit for purpose” and commercially relevant from a cost and supply perspective.

Graphene based additives (GBAs) were produced using a range of graphene grades in resin systems compatible with the epoxy coating products. GBA manufacture was done via a proprietary process demonstrated in both the laboratory and using commercial dispersion equipment. Graphene concentrations in these additives was in the range of 3 – 10%, with most of the balance of the GBA comprised of epoxy resin. Corrosion performance of coatings systems was assessed directly using a static and cyclic salt spray based around the requirements of standards such as ISO 12944:2018. This data was supplemented with mechanical and electrochemical testing.

After success with both laboratory formulated and commercially available solvent based coatings, our interest diversified to water-borne coatings where the formulation of GBAs was modified using raw materials endemic to the water-based sphere of formulation. These proprietary mixtures again were in the range of 3-10% graphene content and focus was given to stability of the GBA and the graphene enhanced coating. Testing included EIS, ISO9227, mechanical testing, and microscopic evaluation, all of which provide valuable supplemental information on coating system performance.

It is important to note that within both solvent based and water based coatings GBA is added to the overall coating formulae at approximately 2% by weight yielding a final graphene loading in the coating of approximately 0.1%. This enables graphene raw material costs to be controlled within the overall coating formulation.

Table 1: Test Methods used in Evaluating Coating Performance.

Standard	Description	Comment	Information Obtained
ISO 9227	Neutral Salt Spray		Scribe Corrosion Creep, Blistering
ISO 12944-6:2018	Annexe B Cyclic Testing (1680 Hrs) Sa2.5	C4 Very High / C5 High Durability	Scribe Corrosion Creep, Blistering
ISO 12944-9:2018	Annexe B Cyclic Testing (4200 Hrs) Sa2.5	Cx High Durability	Scribe Corrosion Creep, Blistering
ISO 4624:2016	Adhesion Testing (Pull-Off)		Pull-off pressure
ISO 16773-1 & 2: 2016	EIS		Film Impedance Measurements over time in test
ASTM D638	Tensile Yield Strength, Elongation and Young's Modulus		Tensile Yield Strength, Elongation and Young's Modulus
	Optical Microscopy		Detail on crack propagation in Epoxy polymers.
TM0404	Cyclic Temperature Crack Evaluation		Crack Resilience under temperature variation.

RESULTS

ISO9227:2017 Neutral Salt Spray

1000-hour salt spray was chosen as a "quick" screening method for identifying graphene types that may show promise in anticorrosive coating applications. From the evaluation of numerous graphene grades, several identified themselves as potentially useful. Initial screening results gave us a clear indication that low dosages of graphene can have an impact on the performance of a typical 2 X 150 micron anticorrosive coating system.

ISO 12944-9:2018 Annexe B Cyclic Testing

In order to evaluate a number of graphene grades, a number of laboratory and commercially available coating variants were subjected to ISO12944-9:2018 Annexe B cyclic testing. This test uses a weekly cycle as described below:

1. QUV 4/4 QUV A at 60 Deg C and condensation at 50 deg C — 3 Days
2. ISO9227:2017 Neutral Salt Spray — 3 Days
3. Freeze Cycle (- 20 Deg C) — 1 Day

The data has been gathered over 9 sets of testing over 6 years and the reliable trend that has emerged is that the presence of the correct grade and dosage of graphene within the coating yields significant improvements in scribe creep results relative to the same unmodified coating of between 26-79%.

Round	Vintage	Standard	Duration (hrs)	Relative scribe creep improvement
A	2020	ISO 9227	1,000	34% 79%
B	2021	ISO 12944	1,680	72%
C	2022	ISO 12944	4,200	42%
D	2022	ISO 12944	1,680	n.m.
E	2023	ISO 12944	4,200	26%
F	2022	ISO 12944	1,680	47%
G	2023	ISO 12944	4,200	32%
H	2024	ISO 12944	4,200	31%
I	2025	ISO 12944	4,200	28% (0.100% Gr) 47% (0.125% Gr)

Figure 3. Rounds of Salt Spray and Cyclic Corrosion Testing of Graphene Enhanced Coatings*

*Multiple rounds incorporating lab test formulae, commercially available coatings and commercially manufactured batches of graphene containing protective coatings.

NACE Standard TM0404:2004
Offshore Platform Atmospheric and Splash Zone New Construction Coating System Evaluation

Typically, this testing regime runs for 252 cycles and has a binary pass/fail result. Our interest lay in further examining the impact of graphene on the polymer system and differentiating the performance by including the metric of time by counting cycles to failure (or cracking).

This quantitative testing was utilized to examine the crack resistance of an epoxy coating that was applied at a thickness of 2,000 micron on standard C-channel steel and subjected to a cyclic environment of -30°C to +60°C. The test pieces were examined on a regular basis until failure. It was found that the reference material, a commercially available, widely used protective coating, cracked after 200 cycles whilst the material dosed with 0.100% graphene lasted a further 64 cycles with a final set of samples at 0.125% graphene not displaying cracking until 296 cycles. This represents a significant improvement of approximately 48% against the commercially available coating reference.

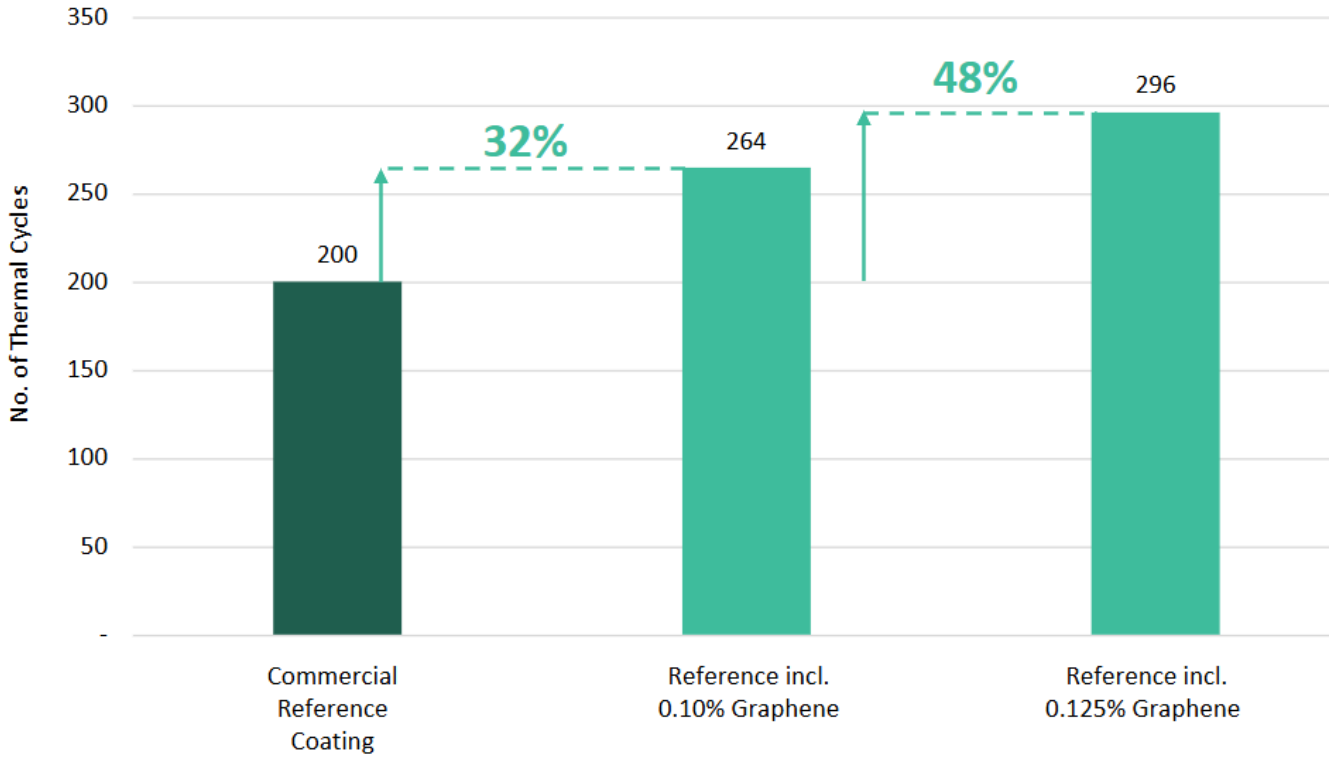


Figure 4. TM0404 Cyclic Crack Resistance Testing through to Failure – 2,000 um DFT

Solid Polymer Elastic Modulus

Filaments of High Density Polyethylene (HDPE) between 2.0 mm and 2.5 mm diameter were produced by melt extrusion and cut to 80 mm length. These were tested at 50 mm span by three-point bend tests on a Salt ST-1000 UTM. Elastic modulus was derived from initial slope data using Salt_UTM Universal Test Machine Software v15.1.0.

The incorporation of graphene significantly increases the elastic modulus in proportion to the dosage rate. Interestingly, and supporting our work in coatings, there is variation in the effectivity of the two graphene grades tested. Our work has shown that there is significant variation in the response of the

HDPE dependent upon a multiplicity of factors including polyethylene grade, graphene grade, dose-response factor and extrusion conditions. Our work in solid polymers demonstrate that the addition of graphene into a polymer yields a strength and resiliency response that is more complicated than just an increase in hardness which deserves further examination.

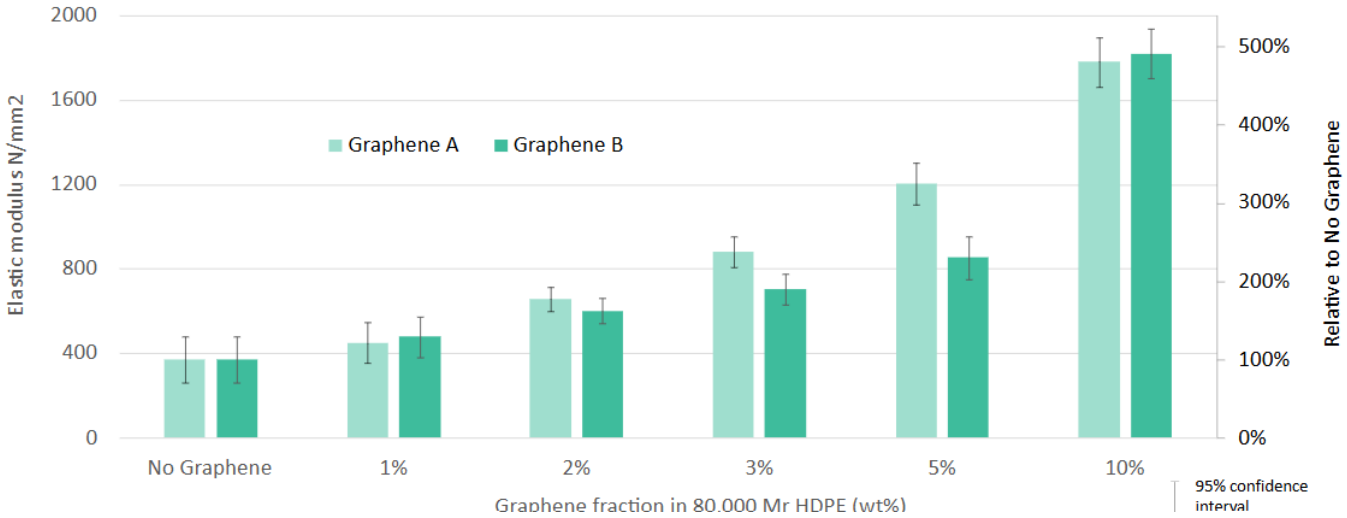


Figure 5. Elastic Modulus for HDPE 80,000 Mr with Graphene A or B (Absolute and Relative to No Graphene), derived from three point bending tests

Water Based Coating Evaluation

The paradigm of reinforcing or supporting a water-based polymer with graphene is similar in principle to that of solvent based. However, there are significant changes in formulation of GBA required and the grades or specific properties of the graphene's that "work" in a solvent based system are different from that of a water based system.

Not surprisingly, the presence of water within the polymer matrix necessitates alternate grades of graphene and proprietary formulation techniques be applied to ensure that the GBAs are both effective and stable as per their solvent borne counterparts. Work to achieve these goals was difficult with the stability of the additives being challenging and evaluation difficult due to the relatively low performance of the acrylic epoxy water based materials.

The test method referred to below is Rapid Electrochemical Assessment of Paint (REAP) which is an accelerated EIS methodology identified and demonstrated by Kendig[3] with success. The 24hr EIS cycle on a scribe is evaluated for creep and then correlated to a theoretical "time to coating failure" in a salt spray environment via an equation derived from data from approximately 200 equivalent experiments.

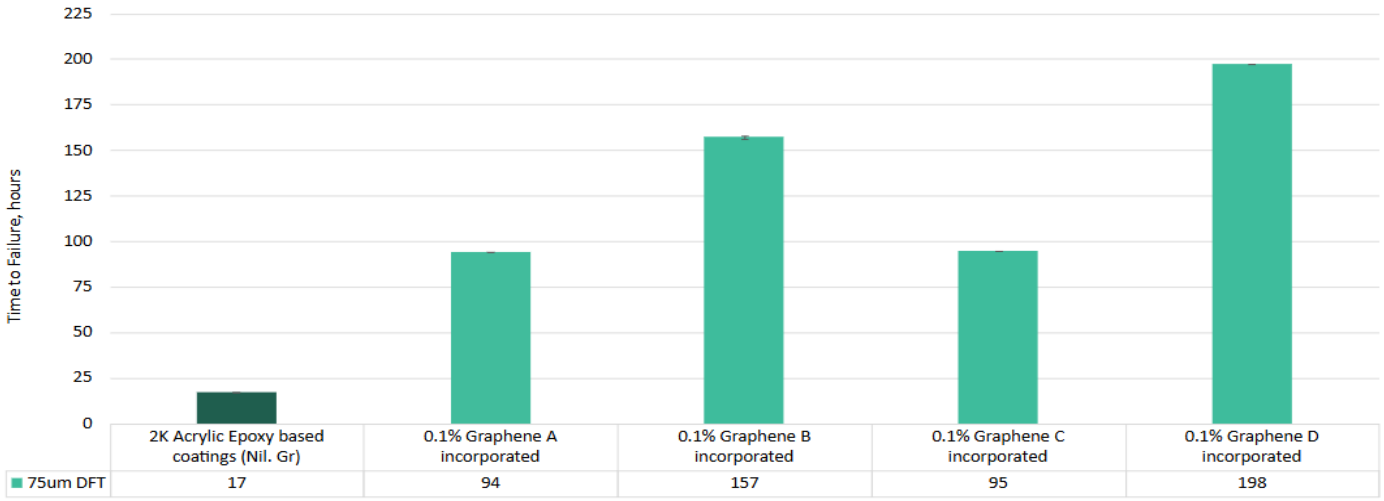


Figure 6. Theoretical Salt Spray Time to Failure (TTF) extrapolated by 24h scribe creep according to Rapid Electrochemical Assessment of Paint (REAP)[3]

The learning obtained from the initial REAP work was then utilized and a commercially available water based 2K epoxy coating was treated with several different grades of graphene, sprayed onto blasted panels at 150 micron and tested under ISO9227 conditions (960 hours). The improvement in scribe creep of up to 44%, is significant and repeatable across multiple panels and demonstrates clearly the benefit of the graphene enhanced coating formulation.

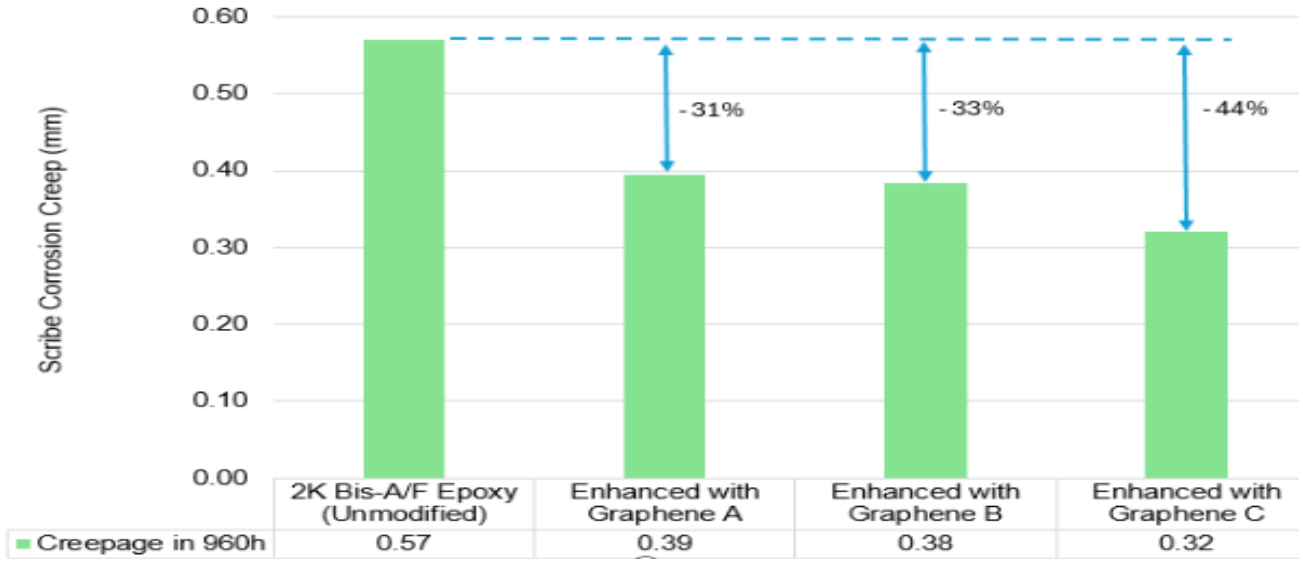


Figure 7. Corrosion Creep - ISO9227 960Hr Salt Spray data of a Commercially Available 2K Bis A/F Epoxy Coating with Alternate Grades of Graphene

CONCLUSIONS

From the data presented it can clearly be seen that the presence of a correctly formulated graphene based additive (GBA) into a high solids epoxy coating has a marked positive effect upon both scribe creep and crack resistance. It is proposed that these and other properties including adhesion and flexibility are improved because of the graphene reinforcing or supporting the inherently brittle epoxy polymer once cured. The increase in the resiliency of the coatings is expected to translate to “in field” performance and to date, a number of field trials are exhibiting the expected behaviours and proportional extensions which would see years added to maintenance events, reducing downtime, costs and CO_2 emissions.

Whilst water based epoxies are not widely utilised in protective coatings as yet, there is also meaningful data supporting significant improvement through graphene incorporation and it is conceivable that a properly formulated graphene enhanced water based epoxy could have its place in the range of environmentally friendly coatings utilised by asset owners.

Vision 2030 is an initiative by the Saudi Arabian government which will promote graphene manufacturers establishing production in region and allow sourcing and manufacture of GBAs and graphene enhanced coatings locally, providing a more sustainable paradigm for local industry. GBA manufacturing processes are modular for fast localization so production ramp-up is not a difficult hurdle to overcome. As a guide, 1.3 tonnes of graphene will enhance ~1 million Litres of paint which will extend maintenance intervals and concomitantly reduce CO_2 emissions from the coating manufacturing, blasting and painting process.

Critical to the adoption of graphene enhanced epoxy coatings by the coatings industry is their ongoing evaluation in laboratory and field trials under a range of conditions and asset owner specific standards. Active participation in the promotion and testing of graphene enhanced coatings by companies such as Aramco is vital to seeing this impactful technology commercialized in the near term.

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