Paper No.
19109

AMPP™
ANNUAL CONFERENCE + EXPO
MARCH 19-23, 2023 | DENVER, COLORADO

# Graphene - Something New for Decades old Epoxy Coating Technology

Andrew Smith
Sparc Technologies Ltd.
51 Rundle Street
Kent Town, South Australia, 5067
Australia

Denis Wright
Sparc Technologies Ltd.
51 Rundle Street
Kent Town, South Australia, 5067
Australia

Grant Mathieson
Sparc Technologies Ltd.
51 Rundle Street
Kent Town, South Australia, 5067
Australia

Andrew Vu
Sparc Technologies Ltd.
51 Rundle Street
Kent Town, South Australia, 5067
Australia

## ABSTRACT

Graphene was first isolated in 2004 and was hailed as a wonder material due to its unique combination of properties. These include large surface area per unit weight, high tensile strength, high modulus of elasticity, good thermal conductivity and electrical conductivity. Practical application has been slow to develop, however almost two decades later, the full potential of this material is being harnessed to enhance products across a broad range of industries. This paper shows how graphene can significantly enhance the performance of functional coatings.

The inclusion of very low levels of effectively dispersed Graphene in high solids epoxy coating formulations has been found beneficial to their anticorrosive performance. This is seen as reduction in scribe corrosion creep and improved adhesion when assessed as part of testing to ISO[(1)] 12944 Annex B. Similar benefits have been observed across a range of epoxy coating formulation types including commercially obtained materials.

An investigation of the mechanism of this improvement largely discounts the contribution of barrier or chemical interactions. It is instead proposed that the observed improvements can be explained by simple mechanical reinforcement of the polymer system, with Graphene particles acting as points of reinforcement or stress relief that limit crack propagation on a micro scale. The propagation and termination of cracking of a Graphene Epoxy system close to fracture surfaces was observed by optical microscopy. Where cracks propagated to a graphene particle, it was commonly observed that the crack terminated at the particle. This suggests wider potential application in high performance coatings where Graphene could improve long term durability by reducing the incidence of cracking.

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

(1) International Organization for Standardization (ISO), Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

## INTRODUCTION

Two component Epoxy polymer systems have been used as the basis for high performance protective coating systems since the 1950s. Numerous Epoxy resin types and ambient condition curing agents are available today which allow great flexibility in the formulation of coating products. This has led to the development of 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 performance properties and limitations. While the basic properties of adhesion, film toughness and general chemical resistance are very important in achieving the required durability in these coatings, performance is often limited by the mechanical properties of the film.
Aside from general corrosion resistance, cracking of protective coatings and linings in service is a key issue in industries where reliable coating performance is crucial. Established formulation techniques such as reduced crosslinking or introduction of diluents to reduce film brittleness and cracking tendency can impact on the overall chemistry of the coating film and invariably lead to some compromise in performance. Any changes of this nature require careful performance evaluation before adoption into commercial products.

Carefully applied Graphene technology provides the ability to improve mechanical properties of a coating film via physical reinforcement of the polymer system and does so without any chemical change to the coating film. This 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 selected Graphene types on the performance of a range of epoxy anticorrosive systems and attempt to determine the mechanism by which this is occurring.

## 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 including of 350 microns or more, including UV durable finishes or antifouling systems.

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 looked at optimization of Graphene levels in a range of Epoxy coating products. Formulation of the coatings was based around Graphene based additives (GBAs) which were produced using a range of Graphene types in resin systems compatible with the coatings product. GBA manufacture was via a proprietary process. The Graphene concentration in these additives was in the range of 3 – 10%, with most of the balance comprised of Epoxy resin. Where experimental coating formulations were used, the GBA was employed as part of the formulation. Where commercially available coatings were used, samples were prepared by post addition of GBAs to the product. In each test series employing this approach, an “Epoxy Blank” was included. This was a coating sample containing no Graphene, but with Epoxy resin added in the amount introduced by the highest additive level in that series. The Epoxy Blank was included to compensate for the effect of the Epoxy brought into the system via the GBA and act as a true baseline for Graphene performance in the test series. In experiments employing varying Graphene levels, each sample had a proportional amount of additional Epoxy resin in order to maintain constant stoichiometry across the sample series.

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

Corrosion performance of coatings systems was assessed directly using a static and cyclic salt spray based around the requirements of ISO 12944:2018. This data was supplemented with mechanical and electrochemical testing.

Other testing includes EIS, water absorption, mechanical testing, and microscopic evaluation, all of which provide valuable supplemental information on coating system performance.

## Standards / Methods Employed

**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 |
| ISO 17463:2022 | EIS - ACET | | Film Impedance following accelerated breakdown. |
| 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. |

## Sample Preparation

For corrosion testing, candidate coating systems were applied to prepared steel panels using standard pressure pot spray equipment, either by a commercial coating contractor in an industrial coating environment or using in house facilities. Coatings used in testing were either laboratory prepared “test bed” formulations, or commercially obtained materials. Graphene was incorporated via Graphene Based Additives as described above.

Initial ISO9227 testing was conducted using 300 X 150 X 1.6 mm cold rolled steel. ISO 12944 Annexe B Cyclic testing was conducted using 150 X 100 X 6 mm hot rolled steel due to the requirement for pull-off adhesion tests. Other tests were conducted using 1.6 mm steel where appropriate.

All panels were first prepared by solvent degreasing, then abrasive blast cleaned with Garnet to surface standard ISO 8501-1 Sa 2.5, with a final surface profile of 35 µm. Surface preparation and coating operations conducted by contractors were monitored by a NACE CIP Level 3 Coating Inspector and the appropriate records are available.

Where required for corrosion assessment, the panels had a scribe introduced according to the requirements of ISO 12944-6 Annex A. For these panels, reverse sides of the panels were coated with a commercial Epoxy Mastic to minimise corrosion during testing and panel edges were provided additional protection by dip applying a thin bead of high solids epoxy coating. All panels were cured for a minimum of two weeks before the commencement of testing.

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

On completion of the specified corrosion testing, panels were washed, dried and photographed. Loose coating around the scribes was removed using a sharp scraper and the panels again photographed. Spread of corrosion was measured with digital Vernier callipers at 0.01 mm precision. Scribe corrosion creep was calculated according to ISO 12944-6:2018 Annex A.

Testing other than the direct corrosion methods was completed in accordance with the stated standards.

## 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 starting set of Graphene grades, several identified themselves as potentially useful. The example below is for one grade in particular and gave us a clear indication that Graphene was capable of having some impact on the performance of a typical 2 X 150 micron anticorrosive system.

**Table 2: Description of Samples used in Figure 1.**

| Sample Code | Description |
|---|---|
| S0008 | Test Bed Epoxy formula (80% Volume Solids, Hydrocarbon Modified, Polyamide cured Epoxy).<br>**Without Graphene**. |
| S0009 | Test Bed Epoxy formula (80% Volume Solids, Hydrocarbon Modified, Polyamide cured Epoxy)<br>**Containing 0.5% Graphene** |
| S0010 | Premium Commercial Epoxy Anticorrosive (60% Volume Solids, Pure Epoxy, Alkylated Phenolic Diamine* cured, Aluminium pigmented). * SDS description |
| S0011 | Commodity Grade Commercial Epoxy Mastic (82% Volume Solids, Hydrocarbon Modified, Polyamide cured Epoxy). |

**Table 3: Test Panels used in Figure 1.**

| Test Panel No. | First Coat (150 Micron) | Second Coat (150 Micron) | Scribe Creep |
|---|---|---|---|
| P0042 | Test Coating – No Graphene | Test Coating – No Graphene | 0.29 mm |
| P0058 | Test Coating - With Graphene | Test Coating – No Graphene | 0.19 mm |
| P0048 | Test Coating – No Graphene | Test Coating - With Graphene | 0.11 mm |
| P0046 | Test Coating - With Graphene | Test Coating - With Graphene | 0.06 mm |
| P0052 | Premium Commercial Epoxy | Premium Commercial Epoxy | 0.13 mm |
| P0056 | Commodity Commercial Epoxy | Commodity Commercial Epoxy | 0.36 mm |
| P0060 | Test Coating - With Graphene | Commodity Commercial Epoxy | 0.28 mm |

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

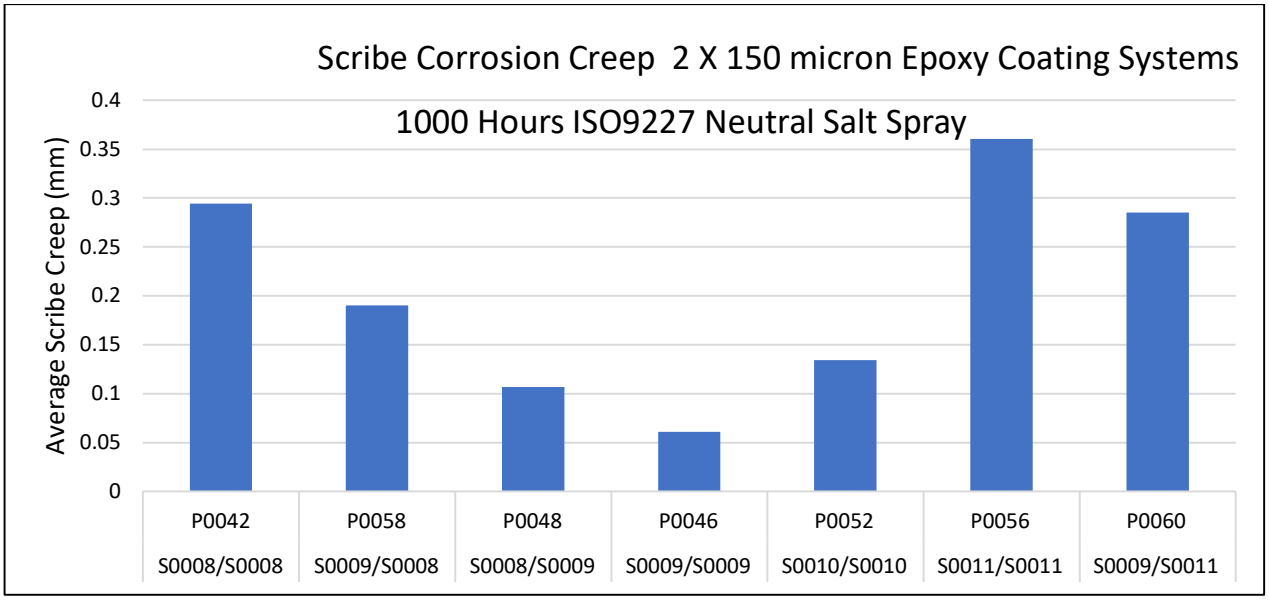



**Figure 1: Average creep of 2 X 150 µm Nominal DFT Coating Systems**

Key observations were that Graphene in either coat gave some improvement in performance, with Graphene in both coats giving the best result. The results for P0048 (No Graphene in first coat, Graphene in second coat) effectively rules out any chemical or passivating effect. Particularly encouraging was the fact that we had taken a low cost product (S0008, Hydrocarbon modified Polyamide Epoxy at 80% volume solids), added a small amount of Graphene and made it perform better in this test than an industry benchmark 60% volume solids pure Epoxy. S0011 was included as an additional reference and is a low cost Epoxy Mastic that is similar in formulation to S0008. S0011 performance can be improved by applying it over a Graphene containing primer – see P0060.

While 1000 hours salt spray would never be considered a rigorous test for this class of coating, the results provided encouragement for additional work.

## ISO 12944-9:2018 Annexe B Cyclic Testing (1680 Hours / 10 Weeks)

In order to determine suitable addition levels of two candidate Graphene grades, a number of sample variants were subjected to 1680 hours (10 weeks) of 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. ISO9227:2017Neutral Salt Spray — 3 Days
3. Freeze Cycle (- 20 Deg C) — 1 Day

Three coat systems were comprised of:

| | |
|---|---|
| Hot Rolled Steel 150 X 100 X 6 mm | Sa 2.5 / SP10 |
| Test bed Epoxy (80% Volume Solids) | 2 X 150 microns |
| Polyurethane finish coat | 50 microns |
| Total | 350 microns |

All panels had a scribe introduced according to ISO12944 requirements

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

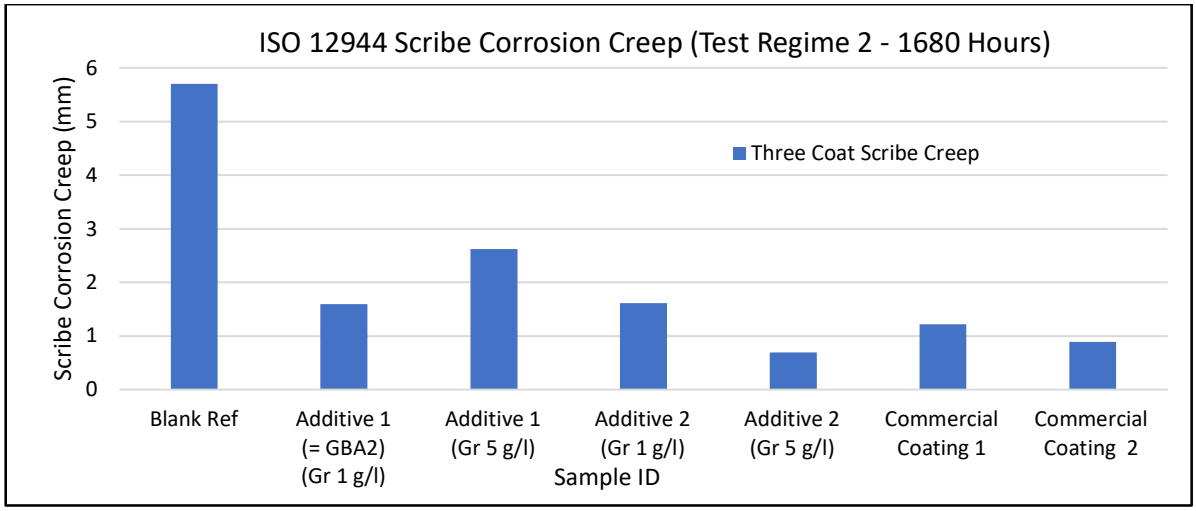



**Figure 2: Average creep of 350 µm Nominal DFT Coating Systems – 1680 Hours**

In this testing, 1 g/l levels of both additives examined gave good performance improvements vs the blank reference. Additive 2 gave further improvement at 5 g/l whereas Additive 1 was worse at this level than at 1 g/l. These results highlight the importance of determining optimum addition rates for each Graphene type.

## ISO 4624:2016 Adhesion Testing (Pull-Off)

The same range of samples was subjected to adhesion testing as a single coat (150 micron) and demonstrated improved adhesion that correlated well with the improvements in corrosion performance. Additive 1 (GBA2 in later work) at 0.1 % Graphene loading in the paint formulation demonstrated the best performance, with a 19% increase in pull-off result vs the unmodified blank. It is important to note that in all cases, the mode of failure was almost exclusively cohesive failure in the coating, so strictly not a measurement of the adhesion of the coating to the steel – rather a measure of the tensile strength of the coating.

**Table 4: Pull-Off Adhesion Values for 150 µm Nominal DFT Coating Films**

| Sample | Pull-Off Adhesion (MPa) | Index vs Blank Reference |
|---|---|---|
| Blank Ref | 14.69 | 1.00 |
| Additive 1 (Gr 1 g/l) | 17.49 | 1.19 |
| Additive 1 (Gr 5 g/l) | 15.98 | 1.09 |
| Additive 2 (Gr 1 g/l) | 14.95 | 1.02 |
| Additive 2 (Gr 5 g/l) | 17.11 | 1.16 |
| Commercial Coating 1 | 12.62 | 0.86 |
| Commercial Coating 2 | 12.71 | 0.87 |

## ISO 12944-9:2018 Annexe B Cyclic Testing (4200 Hours) – Various Coating and Additive Types

The range of testing was further expanded to include 4 Graphene based additives and a range of 5 Epoxy coating types - 4 of which were commercially sourced and the other (Test Epoxy 5) being our in-house test bed coating.

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

**Table 5: Description of Samples used in Figure 3.**

| Coating Designation | Formulation Type |
|---|---|
| Test Epoxy 1 | 82% Volume Solids, Epoxy (solid Hydrocarbon modified), Polyamide cured |
| Test Epoxy 2 | 60% Volume Solids, Phenalkamine Cured High Aluminium |
| Test Epoxy 3 | 85% Volume Solids, Epoxy (solid Hydrocarbon modified), Polyamine adduct cured |
| Test Epoxy 4 | 55% Volume Solids, Pure Epoxy, Polyamide cured, Aluminium pigment |
| Test Epoxy 5 | 80% Volume Solids, Epoxy (liquid Hydrocarbon modified), Polyamide cured. |

All samples based on commercial coatings were prepared by post addition of Graphene based additive (GBA) to existing paint to give 0.1% by weight Graphene in the wet paint. Using this approach, an amount of Epoxy resin is introduced to the system, and this must be taken into account. To this end, an "Epoxy Blank" was used in each case to show the impact of increasing Epoxy content alone by the same amount introduced via the Graphene additive. This removes the Epoxy content as a variable and effectively resets the baseline for the data. The actual impact of epoxy addition on scribe creep varies from product to product. The sample for Test Epoxy 5 was laboratory manufactured from raw materials and therefore did not require an “Epoxy Blank”. The unmodified coating was used as a reference in this case.

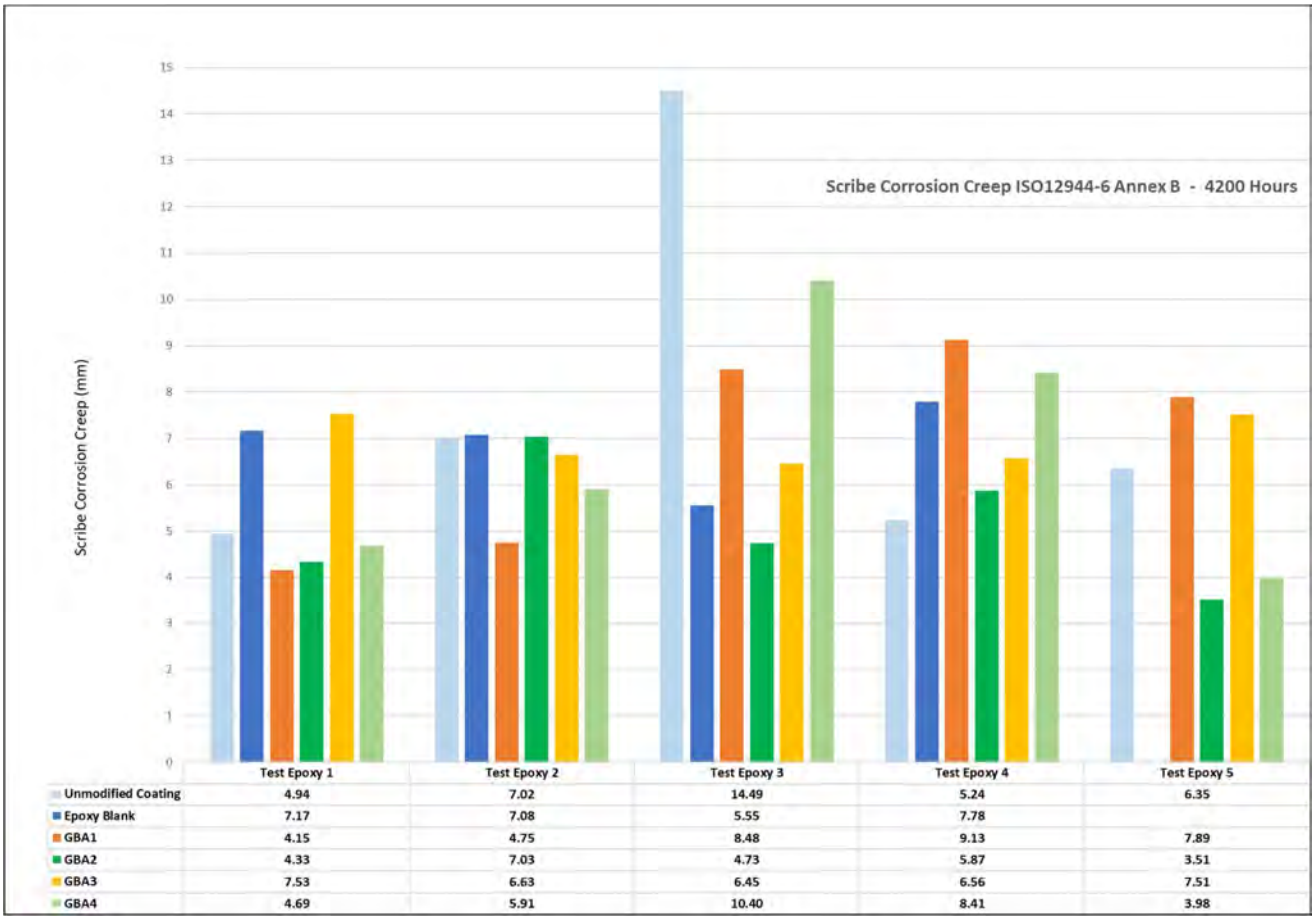
Test panels were prepared as per the 10-week testing discussed above. Results are shown in Figure 3 below. In each case, at least one of the Graphene based additives has imparted significantly better (i.e. lower) scribe corrosion creep values. With one exception (Test Epoxy 2) GBA2 has provided the most improvement in each coating variant.Test Epoxy 2 is recognised as an industry benchmark with good performance largely attributable to a very high Aluminium flake content. It is possible that the smaller particle size in GBA1 is more suited to imparting improvement in this particular coating than is GBA2

This is a very aggressive test for this type of coating system – normally a Zinc rich primer would be used in Cx (offshore) systems. 1680 or 2688 hours perhaps more appropriate as indicative of C4 or C5 Service where this type of coating system would be used, however we were seeking to examine differences in performance rather than absolute compliance with the requirements of the standard. It is interesting to note that Test Epoxy 5 with GBA 2 very nearly meets the performance requirements (i.e. 3 mm scribe creep) for this standard.

## ISO 12944-9:2018 Annexe B Cyclic Testing (1680 Hours) – Fine Tuning of Graphene Level

In order to establish optimum Graphene loading in a specific Epoxy coating system, a test series was run using GBA2 at a range of levels to give Graphene content in the binder component of the coating between 0.04 and 0.21%. The samples were prepared by post addition of GBA2 and requisite Epoxy resin corrections to a commercially obtained Epoxy Coating product – in this case, an 85% volume solids Amine cured Epoxy applied at 250 microns in a single coat. The Epoxy corrections were used to ensure that each sample had the same amount of Epoxy addition. As in other work, an “Epoxy Blank” was used as a secondary baseline for testing. See Figure 4 below. It can be seen that for this product, addition of Epoxy alone has an adverse effect on corrosion resistance, however this is reversed when Graphene is present at all levels tested.

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).




| | Test Epoxy 1 | Test Epoxy 2 | Test Epoxy 3 | Test Epoxy 4 | Test Epoxy 5 |
|---|---|---|---|---|---|
| Unmodified Coating | 4.94 | 7.02 | 14.49 | 5.24 | 6.35 |
| Epoxy Blank | 7.17 | 7.08 | 5.55 | 7.78 | |
| GBA1 | 4.15 | 4.75 | 8.48 | 9.13 | 7.89 |
| GBA2 | 4.33 | 7.03 | 4.73 | 5.87 | 3.51 |
| GBA3 | 7.53 | 6.63 | 6.45 | 6.56 | 7.51 |
| GBA4 | 4.69 | 5.91 | 10.40 | 8.41 | 3.98 |

**Figure 3: Average creep of 350 µm Nominal DFT Coating Systems – 4200 Hours**

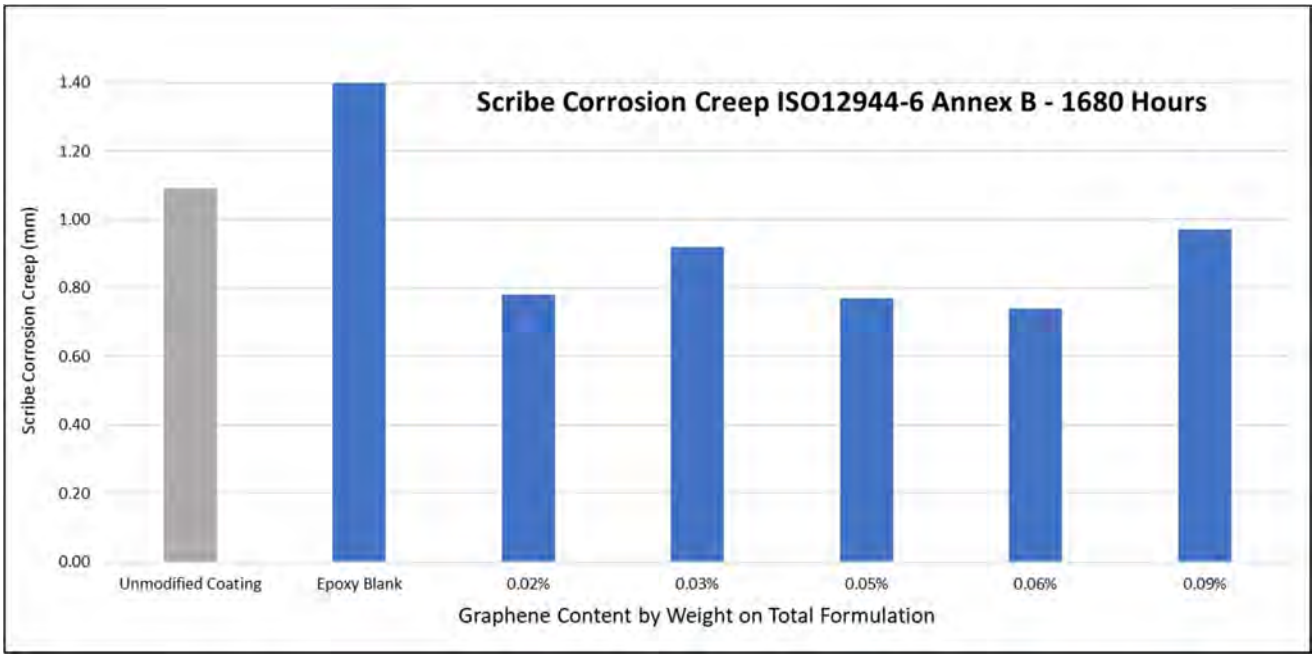



**Figure 4: Average creep of 250 µm Nominal DFT Single Coat System – 1680 Hours**

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

The resistance of the paint films to scribe corrosion creep was improved by the addition of Graphene at a range of levels. Scribe creep was reduced by 47% vs Epoxy Blank at 0.06% Graphene, however significant improvement (44%) was seen at the lowest Graphene level (0.02%) tested and it is possible that the optimum for this particular coating may be lower than this.

## ISO 17463:2022 EIS – Accelerated Cyclic Electrochemical Technique (AC/DC/AC)

In seeking to investigate potential improvements in corrosion protection provided by the incorporation of Graphene into Epoxy coatings, the protective ability of the coating variants was assessed using the Accelerated Cyclic Electrochemical Technique (i.e., ACET or AC/DC/AC)) in combination with the Immersion Technique. This combination is intended to accelerate degradation of the coating and measure the impact of this over time.

Three coating variants were assessed:

Base Coating Type: Commercially sourced immersion grade Hydrocarbon modified Epoxy Polyamide coating (82% Volume Solids). The Graphene used was coded AAV and incorporated via GBA2 additive.

- Unmodified Coating
- Epoxy Blank (see earlier discussion)
- Graphene Modified Coating (0.1% Graphene by weight on total formulation).

Apparatus used: Gamry [(2)] Interface 1010E, Graphite counter electrode, Ag/AgCl (KCl Saturated) Reference electrode, Paint Test Cell (PTC1). Electrolyte: 3.5% NaCl in RO Water.

Coating dry film thickness 150 microns applied to steel panels prepared as for corrosion testing.

The coating samples on carbon steel acting as the working electrode were immersed in the 3.5% wt. NaCl solution in a three-electrode electrolyte cell with graphite as the counter electrode and Ag/AgCl (saturated KCl) electrode as the reference electrode. See Figure 6.

The ACET test was carried out in the steps shown in Figure 5. The ACET cycle was repeated 6 times, then the panel left in immersion at room temperature. The 6 X ACET cycles were repeated on a weekly basis until obvious disruption of the coatings' parameters were observed.

**Step 1**: Initial measurement for EIS of the paint film.

**Step 2**: apply cathodic polarisation at -4V versus $E_{Coor}$ for 30 minutes.

**Step 3**: Apply Anodic polarisation at +4 Volts versus $E_{Coor}$ for 30 minutes.

**Step 4**: relaxation - monitoring the OCP (Open Circuit Potential) in 2.5 hours while the system regains its stability.

**Step 5**: Measure EIS again, then repeat step 2

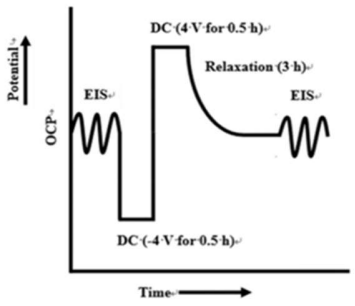



**Figure 5: Polarisation Cycle for ACET Method (Gamry)**

[(2)] Gamry Instruments, Inc., 734 Louis Drive, Warminster, PA 18974, USA

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

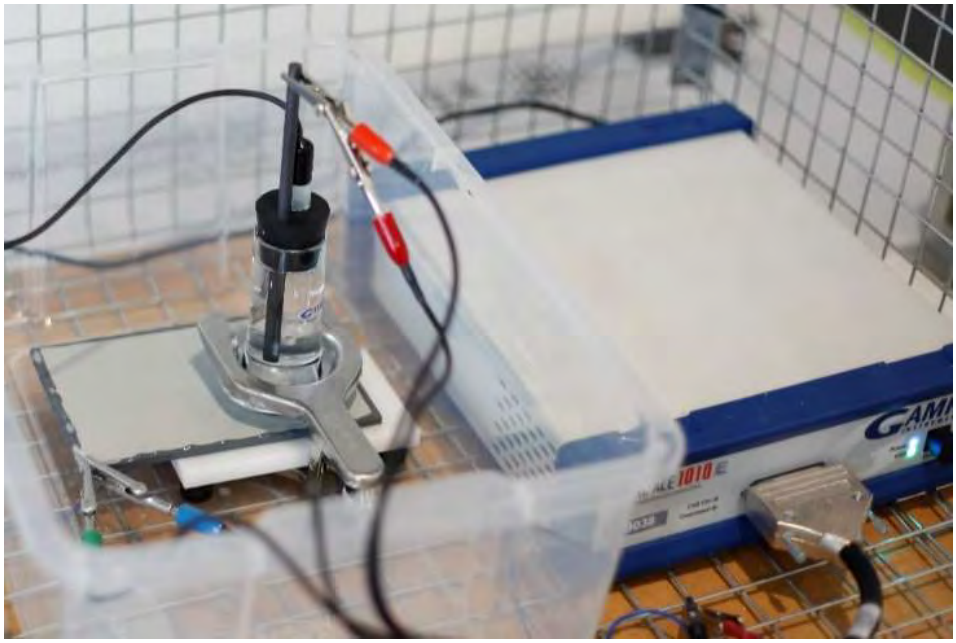


**Figure 6: Test Cell for ACET Method**

The equivalent circuit as shown in Figure 7 was used to analyse the EIS spectra measured during the ACET tests. The elements of the circuit can be associated with the coating performance, which have the meanings shown:

**$C_c$**: constant phase element of the capacitance of the coating

**$C_{cor}$**: constant phase element of the double layer capacitance of the substrate metal exposed in the pores or defects of the coating,

**$R_{cor}$**: polarisation resistance of the substrate metal exposed in the pores or defects of the coating.

**$R_{po}$**: resistance of the pores/defects in the coatings or the coating resistance

**$R_{soln}$**: electrolyte resistance

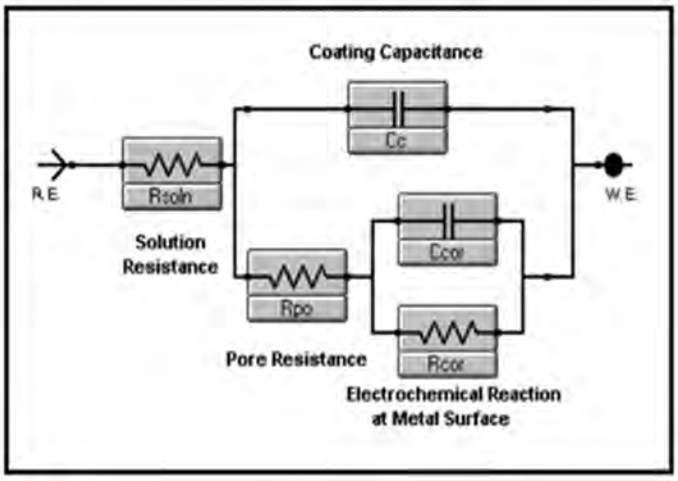



**Figure 7: Circuit Model for Coated Steel Panels in Immersion (Gamry)**

Pore Resistance, $R_{po}$, is a measure of the porosity and deterioration of the coating. $R_{po}$ values are usually related to the number of pores or capillary channels to the substrate surface through which are short-cuts for the electrolyte to reach the coating / substrate interface. Hence, $R_{po}$ usually decreases with time, however can be reversed when the defects are blocked by corrosion products such as the metal oxides/hydroxides and/or hydrogen bubbles (Yuquing, 2021).

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

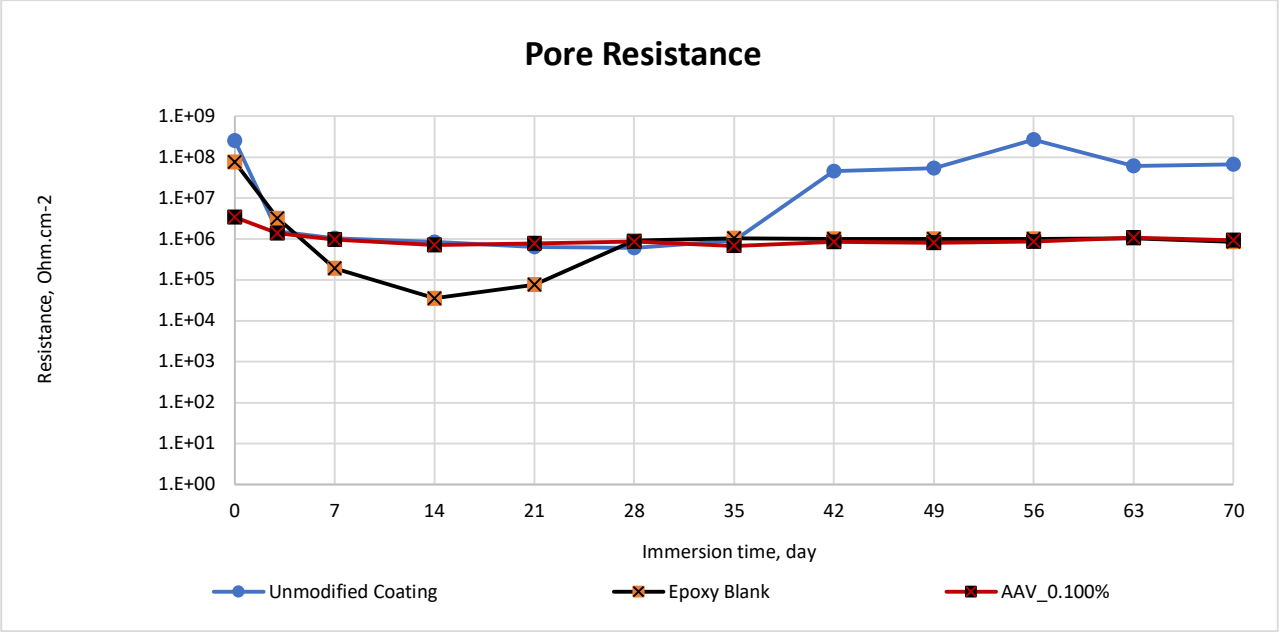



**Figure 8: Pore Resistance ($R_{po}$) vs Time in Immersion**

The starting point Pore Resistance ($R_{po}$) for each sample was different, with Unmodified Coating > Epoxy Blank > 0.1% Graphene, indicating that the addition of Epoxy resin alone increases the starting point $R_{po,}$ and the inclusion of Epoxy and Graphene reduces it. $R_{po}$ average baseline was in general decreasing throughout the test, implying that the ingress of water into the coating and the corrosion of the substrate has occurred to some extent in all samples. The $R_{po}$ increased in some instances is explainable by considering that the pores or defects in the film are being blocked by corrosion products in the coating degradation process (Gimeno, 2014).

$R_{po}$ of all samples dropped from the beginning of the test, reaching the average baseline at around 3 days. The $R_{po}$ of the Unmodified Coating and the Graphene modified coating levelled out to follow the average baseline, however the Epoxy Blank continued to decline, reaching a minimum at around 14 days then increasing to the average baseline at 28 days. These observations indicate more rapid ingress of electrolyte through the Epoxy Blank paint film, with corrosion of the substrate steel starting at around day 14. Pore blockage appears largely complete by day 28, due to the difference in the resistances and conductivities of corrosion products formed by ACET processes (Dajiang, 2021).

The Unmodified Coating showed quite a satisfactory performance against the ACET and Immersion test, with the increase in its $R_{po}$ value only observed from day 42 onwards. Beyond this, the increase in $R_{po}$ values could be explained by the forming of corrosion products, with the protective properties of the coating system being diminished by the repeated ACET polarisation cycles.

The modified sample with 0.100% Graphene loading showed improved inhibition on the permeation of water through the paint film. The migration of water to the steel substrate and which causes the induction of corrosion was not observed even at the 70th day of the test, as demonstrated by the high stability of the $R_{po}$ values obtained from the EIS measurements. The corrosion protection in this test has been significantly improved by the inclusion of 0.1% Graphene.

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

## ASTM D638 Tensile Yield Strength, Elongation and Young's Modulus

Mechanical testing was performed on free coating films at the Smart Materials Laboratory, Swinburne University of Technology in Melbourne, Australia.

Three coating variants were assessed: Base Coating Type: Commercially sourced immersion grade Hydrocarbon modified, Epoxy Polyamide coating (82% Volume Solids). The Graphene used was incorporated via GBA2 additive.

- Unmodified Coating
- Epoxy Blank (see earlier discussion)
- Graphene Modified Coating (0.1% Graphene by weight on total formulation).

Free films were generated by drawing down 200 micron wet films onto Teflon sheet and removing once cured. The resulting 150 micron nominal dry film thickness films were then cut to size and aged for two weeks at 25 deg C before submitting for test. 5 samples of each variant were tested, and the results presented as an average of those. See Table 6 below.

**Table 6: Mechanical Data for Graphene Modified Coating Films**

| Sample Code | Description | Tensile Strength (MPa) | Extn at Break (mm) | Modulus (GPa) |
|---|---|---|---|---|
| **S0201** | **Unmodified Coating** | **17.117** (± 1.298) | **0.00339** (± 0.00028) | **5.577** (± 0.175) |
| **S0202** | **Epoxy Blank (EB)** | **16.336** (± 1.873) | **0.00335** (± 0.00049) | **5.346** (± 0.148) |
| **S0197** | **0.1% Graphene** | **23.578** (± 2.089) **44% Increase vs EB** | **0.00679** (± 0.00107) **103% Increase vs EB** | **4.808** (± 0.130) **10% Decrease vs EB** |

## Optical Microscopy of Fractured Graphene Modified Epoxies

Increased mechanical strength of cured two-part epoxy resin due to inclusion of graphitic nanoparticles has been reported (Li, 2017). Recently, descriptions of the way in which graphene acts to achieve the improvement in this system have been suggested (Abdolmajid Alipour, 2021), mostly via SEM but with some optical microscopy of microcracks in tensile tested samples. Optical microscopy of termination and bridging of microcracks in hydroxyapatite by reduced graphene oxide (rGO) has been reported (Lu, 2013). By observing the propagation and termination of microcracks arising in the vicinity of a fracture surface with an optical microscope, a better understanding of how the increased strength of graphene-epoxy systems comes about can be reached.

The composite was 0.05 weight % Graphene nanoplatelets in Liquid Epoxy Resin, made by combining GBA2 (proprietary Graphene based additive) with pure resin, then curing with 125 grade Polyamide at near stoichiometric proportions. The complete mixture was loaded into standard silicone dog-bone moulds (as used for making mechanical strength testing samples), degassed in a vacuum chamber for 10-15 minutes, and left to cure overnight at 25°C. After removal from the moulds, samples were post-cured at 50°C for one week. Thin pieces that had extruded from the mould while uncured were fractured by hand and the fractured surfaces were left unpolished. Samples for mounting on glass slides were made by cutting a few mm away from the fractured surface and fastening the resulting sliver to the slide with the fractured face up.

The microscope used was a Nikon[(3)] LV100POL, housed at the Adelaide Microscopy Unit of the University of Adelaide's City Campus. For focus stacking, Nikon[(3)] proprietary software NIS-Elements was used.

[(3)] Nikon Australia Pty. Ltd.. Suite 501, Level 5, 5 Rider Boulevard, Rhodes NSW 2138, Australia.

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

Figures 9 (a) and (b). show the propagation and termination of cracks close to the fracture surface of the cured composite. Figure 9(a) shows that where cracks propagated to a graphene particle, it was commonly observed that the crack terminated at the particle. Figure 9(b) is at higher magnification of the same view which show additional detail.

It is not yet clear what Graphene types and concentrations provide maximum effect or optimization of mechanical properties and this will be the subject of future investigations. It appears clear that thorough dispersion of the Graphene in the polymer system is important in obtaining maximum benefit.

Calculations estimate that at 0.05% by weight Graphene in polymer, for the range of particle sizes under evaluation, and at full dispersions, there will be between 0.2 – 3 billion discrete particles present per $cm^3$ of polymer, providing a vast network of stress relief and reinforcement points in the polymer matrix.

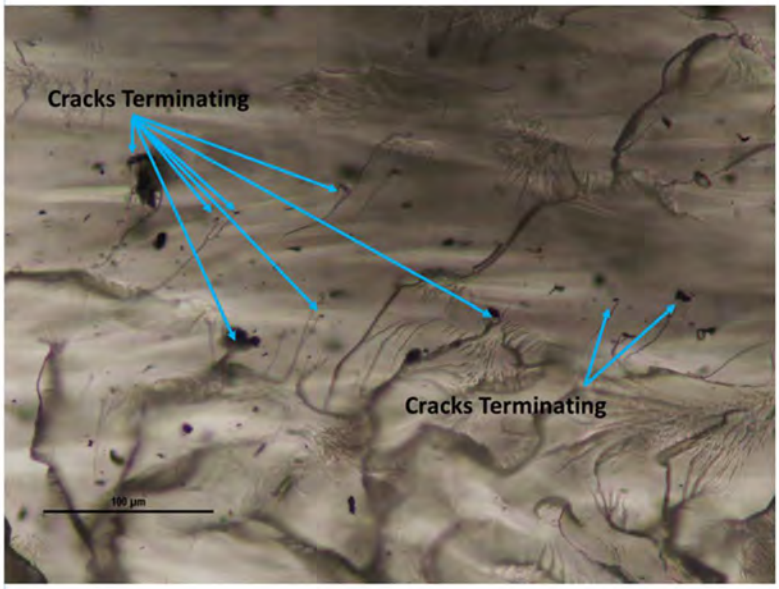



**Figure 9(a)**

Fractured surface of Graphene modified Epoxy at moderate magnification showing termination of cracks at Graphene particles.

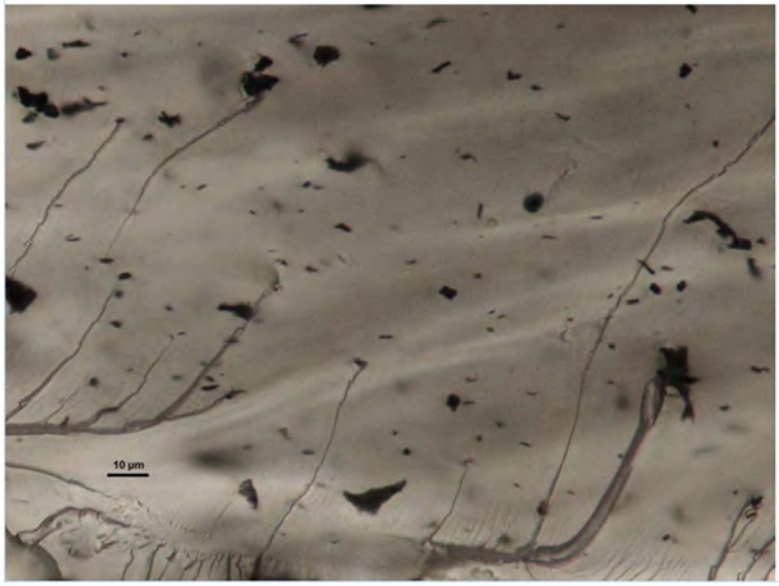



**Figure 9(b)**

Fractured surface of Graphene modified Epoxy at high magnification.

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

## CONCLUSIONS

### Corrosion and Adhesion Testing

Initial screening tests identified various specific Graphene types which appeared capable of improving the performance of Epoxy anticorrosive coatings at very low addition levels. Early work in two coat systems demonstrated that improvement could be obtained by inclusion of Graphene in either coat, with best results when in both coats. This led to the conclusion that the mode of action does not involve any direct chemical interaction with the substrate metal.

Repeated rounds of testing established that performance benefits were achievable across a wide range of formulation types. While a default addition level of 0.1% Graphene on total formulation appeared to reliably improve performance across a range of high solids epoxies, experiments at refinement showed good results at significantly lower levels for some specific coating grades.

### Electrochemical Impedance Spectroscopy

Graphene present at the 0.1% level in and Epoxy coating provided improved performance in EIS/ACET/ Immersion testing, with initially lower and more stable Pore Resistance throughout the test. This suggests that Graphene is aiding in maintaining film integrity through the numerous ACET cycles and continuous immersion.

### Mechanical Testing

Standard tensile testing of Epoxy coating films has shown significant improvement in tensile strength and elongation at break in Graphene modified samples. Combined with lower Youngs modulus this suggests a tougher, more resilient and less brittle film. Apart from assisting in resistance to scribe corrosion creep, these properties could provide benefit in other areas of commercial interest in the protective coatings area such as crack resistance.

### Photomicrography

Microscopic examination of fractured polymer systems indicates that Graphene is likely to be playing a part in reducing crack propagation in stressed epoxy polymer systems. This observation could be used to explain all of the observed improvements in coating performance - reduced scribe creep, maintenance of good pore resistance in ACET testing, maintenance of lower water absorption over time and improved mechanical properties.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge their colleagues Matt Ball and Rafael Enriquez for their valuable assistance in completing the laboratory work necessary to produce this paper. We would also like to thank University of Adelaide and Swinburne University of Technology for their assistance.

© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.
Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

## REFERENCES


1. ISO 9227:2017 Corrosion tests in artificial atmospheres — Salt spray tests

2. ISO 12944-6:2018 Paints and varnishes — Corrosion protection of steel structures by protective paint systems — Part 6: Laboratory performance test methods

3. ISO 4624:2016 Paints and varnishes — Pull-off test for adhesion

4. ISO 16773-1:2016 Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens — Part 1: Terms and definitions

5. ISO 16773-2:2016 Electrochemical impedance spectroscopy (EIS) on coated and uncoated metallic specimens — Part 2: Collection of data

6. ISO 17463:2022 Paints and varnishes — Guidelines for the determination of anticorrosive properties of organic coatings by accelerated cyclic electrochemical technique. Retrieved from ISO: https://www.iso.org/standard/81404

7. Gamry. Retrieved from: https://www.gamry.com/application-notes/corrosion-coatings/accelerated-cyclic-electrochemical-technique/ November 2022

8. ASTM D570-98(2018) Standard Test Method for Water Absorption of Plastics

9. ASTM D638-22 Standard Test Method for Tensile Properties of Plastics

10. Dajiang Zheng, Q. G.-L. (Volume 159, October 2021). Modified AC-DC-AC method for evaluation of corrosion damage of acrylic varnish paint coating/Q215 steel system. Progress in Organic Coatings, 106401.

11. M.J. Gimeno, S. R. (Volume 77, Issue 12, Part A, December 2014). Anticorrosive properties enhancement by means of phosphate pigments in an epoxy 2k coating. Assessment by NSS and ACET. Progress in Organic Coatings, Pages 2024-2030.

12. Yuqing Xu, Guang-Ling Song, Dajiang Zheng, Zhenliang Feng. (2021). The corrosion damage of an organic coating accelerated by different AC-DC-AC tests. Engineering Failure Analysis, Volume 126, 105461.

13. Abdolmajid Alipour, R. L. (2021). Effects of graphene network formation on microstructure and mechanical properties of flax/epoxy nanocomposites. Journal of Materials Research and Technology, 4610-4622.

14. Li, Y. &.-H. (2017). Graphite Nanoplatelet Modified Epoxy Resin for Carbon Fibre Reinforced Plastics with Enhanced Properties. Journal of Nanomaterials, 1-10.

15. Lu, Y. &. (2013). Synthesis of hydroxyapatite-reduced graphite oxide nanocomposites for biomedical applications: Oriented nucleation and epitaxial growth of hydroxyapatite. J. Mater. Chem. B., 1826-1834.



© 2023 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).