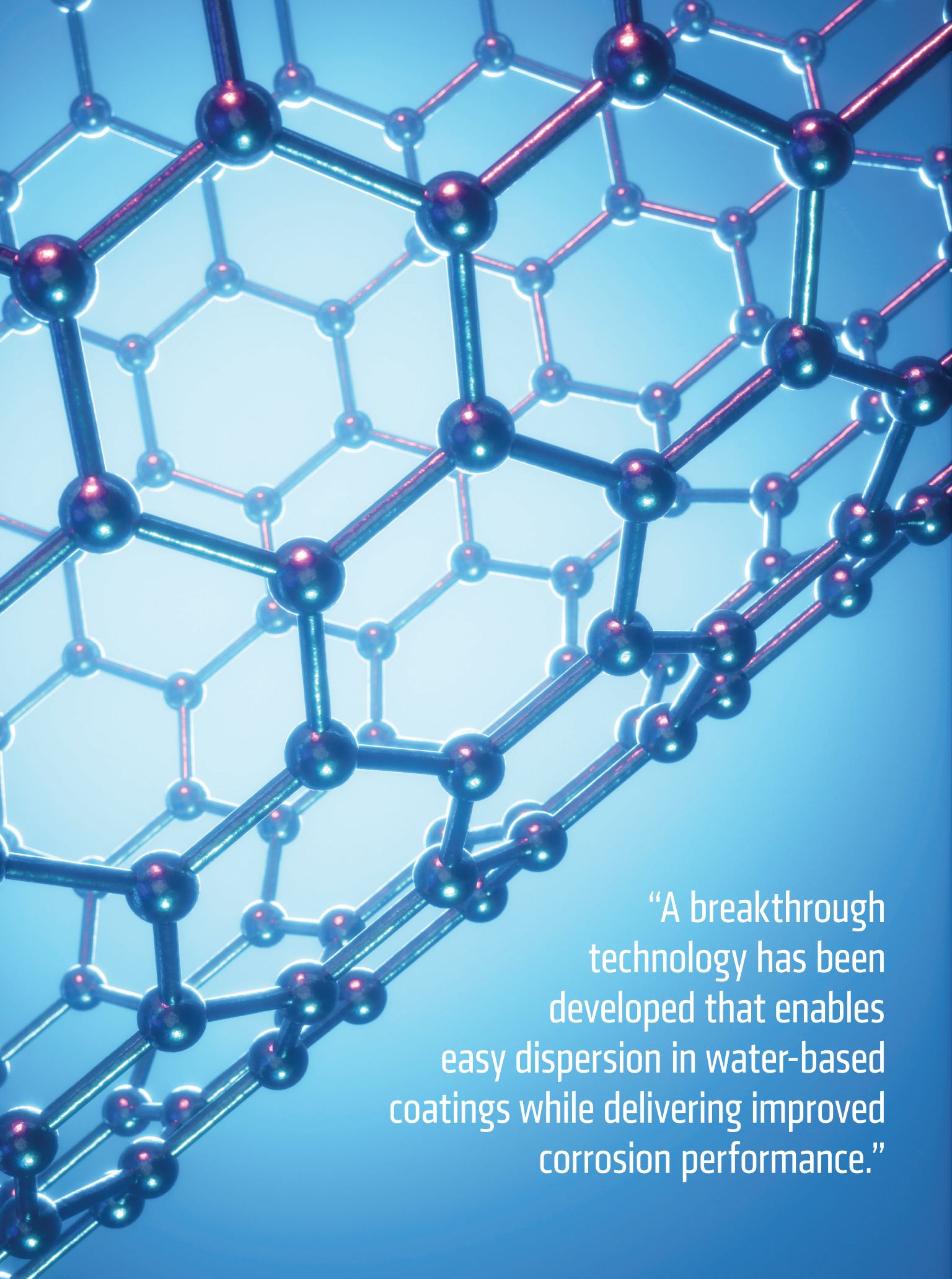


"A breakthrough technology has been developed that enables easy dispersion in water-based coatings while delivering improved corrosion performance."

Waterborne Epoxy Coating: Lifting Performance for Tomorrow

By Adrian Potts, CEO, Applied Graphene Materials

Graphene as a two-dimensional nanomaterial has been extensively researched as a new additive to improve barrier performance, reduce corrosion and extend service life in protective coatings. Previous results have demonstrated significant uplifts in anticorrosive performance in solvent-based coatings using graphene nanoplatelets (GNPs), presenting new opportunities for improved protective coatings with extended service life.

However, 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 anticorrosion performance to that seen in solvent-based systems.

To date, dispersion of graphene in water-based systems has been problematic, causing coating instability or requiring large amounts of surfactant. A breakthrough technology has been developed that enables easy dispersion in water-based coatings while delivering improved corrosion performance. This development provides an important step to raising waterborne coatings' anticorrosion performance and use.

INTRODUCTION

The development of solvent-based epoxy primer systems utilizing graphene nanoplatelets that demonstrate increased performance life[1] has previously been reported. It has been demonstrated that GNPs, when incorporated into an organic coating system, provide a highly tortuous pathway that acts to impede the movement of corrosive species toward the metal surface[2], a passive corrosion protection mechanism as demonstrated by decreased water vapor transmission rates[3], indicating a barrier mechanism.

Waterborne technology has seen growth as interest in products with reduced environmental impact has increased. This is evidenced by increasingly stricter environmental regulations and growing end user demand for environmentally friendly technology.

For this work, we report on the development of a stable and easily incorporated graphene dispersion together with the benefits of incorporation into a water-based primer. A major challenge to the use of graphene nanoplatelets is their dispersion and stabilization. GNPs, in presenting a significant surface area, pose a challenge to colloidal stability and aggregation. Electrostatic or steric mechanisms may be used to achieve stability[5,6]. Water poses a challenging environment for dispersion given the low chemical functionality, hydrophobicity and large surface area of graphene.

We report an assessment of anticorrosion performance using a stabilized aqueous GNP dispersion in a water-based epoxy paint, using complementary techniques: neutral salt spray testing (NSS) and electrochemical AC impedance spectroscopy (EIS).

EXPERIMENTAL PROCEDURE

Dispersion Development and Testing

Stabilization of a colloid in water may be achieved through non-covalent modification of GNPs by use of surfactants. Several studies have been carried out on the effectiveness of surfactants[5,6,7]. Insufficient stabilization may result in coagulation or aggregation of the paint, whereas too high a level may result in water sensitivity.

The authors have developed a resin-supported stabilized dispersion with a graphene loading of 0.5% by weight. This aqueous dispersion has reproducible quality with excellent stability and shows no agglomeration or sedimentation effects. Four batches were manufactured, with repeatable density, viscosity, and particle-size distribution, which are reported in the Results section of this article.

Material & Sample Preparation

GNPs containing prototype primer formulations are detailed in *Table 1*. The three formulations were adjusted for PVC equivalency. Full panel preparation details are shown in *Table 3*.

PVC was maintained at a similar level by reducing the levels of coloring pigments and filler (titanium dioxide, red and black iron oxide, and barytes). The level of talc was left at roughly the same loading (~5%) as this is a platelike pigment which can contribute to the barrier properties of the coating. All systems were maintained at a stoichiometry of 75% (amine: epoxy). Paints were manufactured using a high-speed disperser.

A range of tests were carried out to determine suitability of the graphene modified water-based primers for use as anticorrosive primers, including:

- Neutral Salt Spray (NSS)—ISO 9227
- Electrochemical Impedance Spectroscopy (EIS). All electrochemical measurements were recorded using a Gamry 1000E potentiostat in conjunction with a Gamry ECM8 multiplexer.

In terms of dispersion characterization, the dispersions were made using the following methods:

- Particle size analysis determined using differential light scattering
- Viscosity as measured by a Kinexus Rheometer
- Storage stability characterized using a Turbiscan® Lab Expert stability analyzer

TABLE 1—Paint Formulations

PART A: EPOXY BASE				
Item	Raw Material	Weight %		
		Control System	5% GNP Dispersion System	10% GNP Dispersion System
1	Beckopox EP 2384w/57WA	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	Beckopox VEH 2188w/55WA	13.12%	13.85%	14.48%
14	Water	1.54%	1.64%	1.70%
Total =		100.00%	100.00%	100.00%

Note: Weight percentages are based on the full system loading, Part A + Part B

TABLE 2—PVC and GNP Loadings

PVC	31.47%	31.47%	31.48%
GRAPHENE LOADING (BY WEIGHT)	0.00%	0.025%	0.05%

TABLE 3—Panel Preparation

SUBSTRATE	COLD ROLLED STEEL
Dimensions	152 mm by 101 mm
Preparation	Grit blasting to SA2-1/2, acetone degreases
Grit	Irregularly shaped chrome/nickel shot
Application	Steel drawdown bar (300 µm)
Coating thickness	DFT 80 – 100 µm
Curing	7 days at room temperature (25 °C)

TABLE 4—Particle-Size Distribution

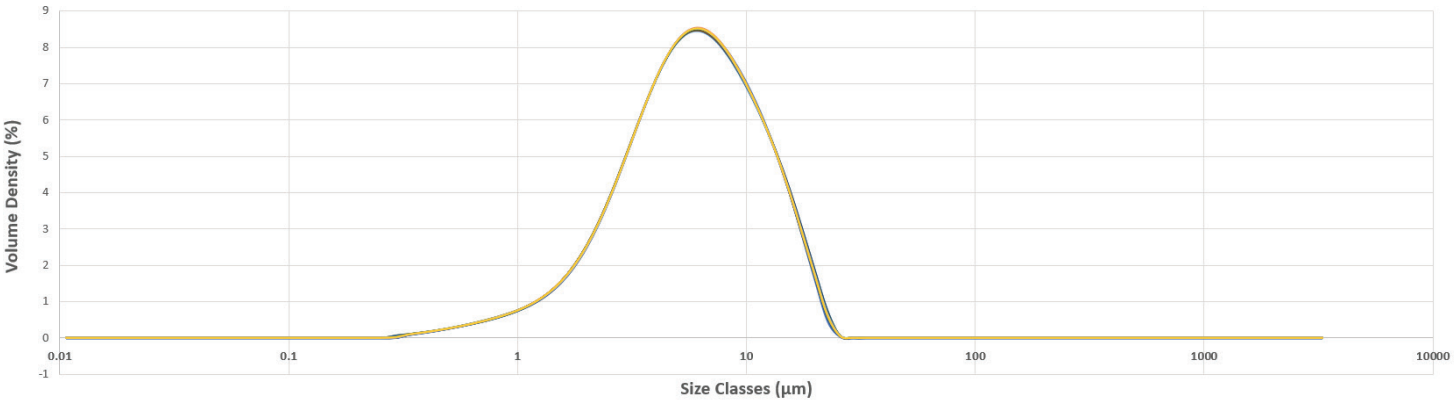
BATCH NUMBER	D10 (MM)	D50 (MM)	D90 (MM)
Batch 1	2.21	6.25	16.58
Batch 2	2.11	5.76	13.57
Batch 3	2.17	6.13	16.13
Batch 4	2.11	5.85	13.7

RESULTS

Dispersion Particle Size

Four batches were manufactured to assess reproducibility and quality of the aqueous GNP dispersions. Particle size is monitored using differential light scattering (DLS) to obtain information on how well dispersed the platelets are within the matrix, as shown in *Table 4* and *Figure 1*. *Figure 2* demonstrates monomodal distribution while the lateral dimensions of the platelets are in the micron scale, the GNPs are typically 3 to 6nm thick.

FIGURE 1—Typical Particle Size Profile as Determined by DLS



Rheology

All four dispersions had a low, pourable, and repeatable viscosity (*Figure 2*). *Figure 3* shows three repeat measurements of the same batch of dispersion, demonstrating a drop in viscosity with increasing shear rate, suggesting that dispersions are shear thinning. Viscosity was measured at 25 °C using a Kinexus Rheometer.

Turbiscan Analysis

Four additional batches were manufactured for stability testing. Stability of the dispersion was characterized using static multiple light scattering. A Turbiscan Lab Expert stability analyzer was used to monitor stability of the aqueous GNP dispersions over a period of 307 days under ambient laboratory conditions.

The Turbiscan measures degree of aggregation, agglomeration, sedimentation, or phase separation through changes in transmission (T) and backscattering (B) 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 summarizes the evolution of transmission and/or backscattering light. Ultimately, TSI corresponds to a cumulative sum of all the backscattering or transmission variation of the entire sample. Results are shown in *Figure 4* while relative values of TSI in respect of stability are given in *Figure 5*.

FIGURE 2—Viscosity Consistency Across Batches

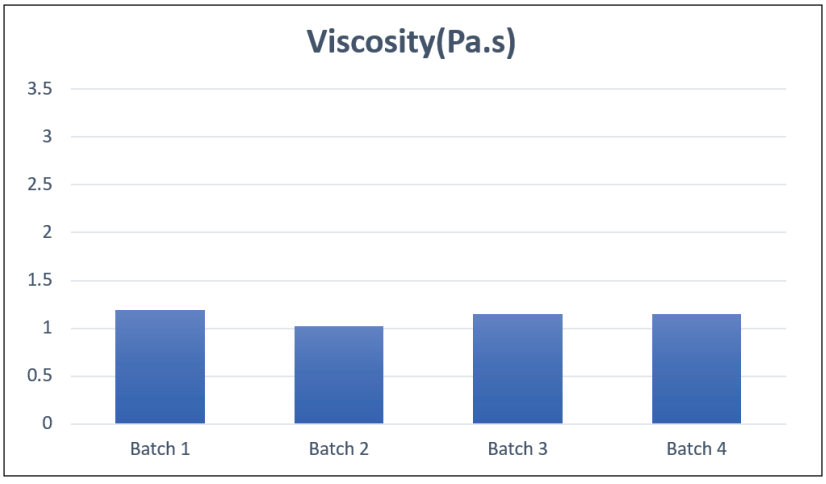


FIGURE 3—Shear-Thinning Behavior of GNP Dispersion

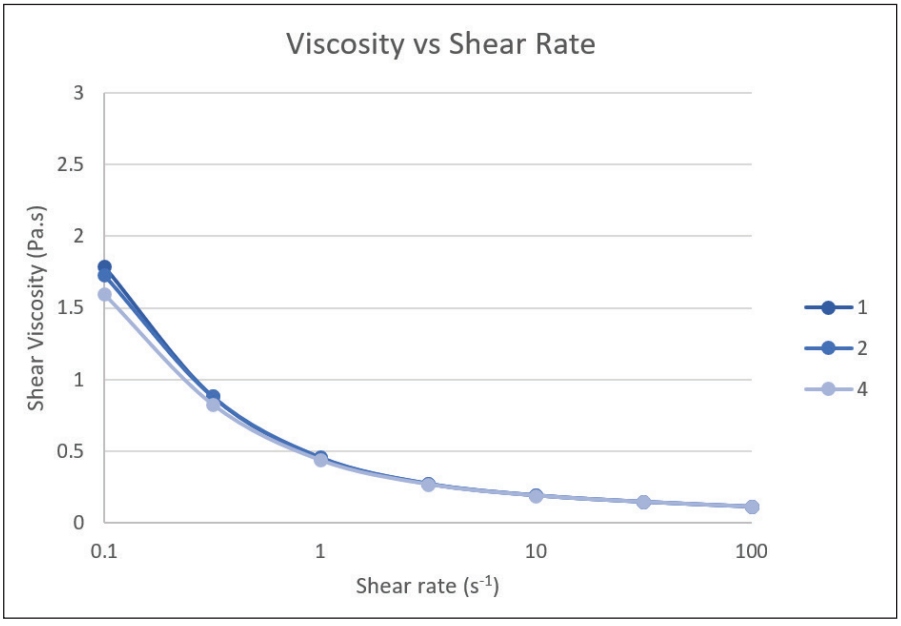


FIGURE 4—Stability of GNP Dispersion Using Turbiscan Stability Index

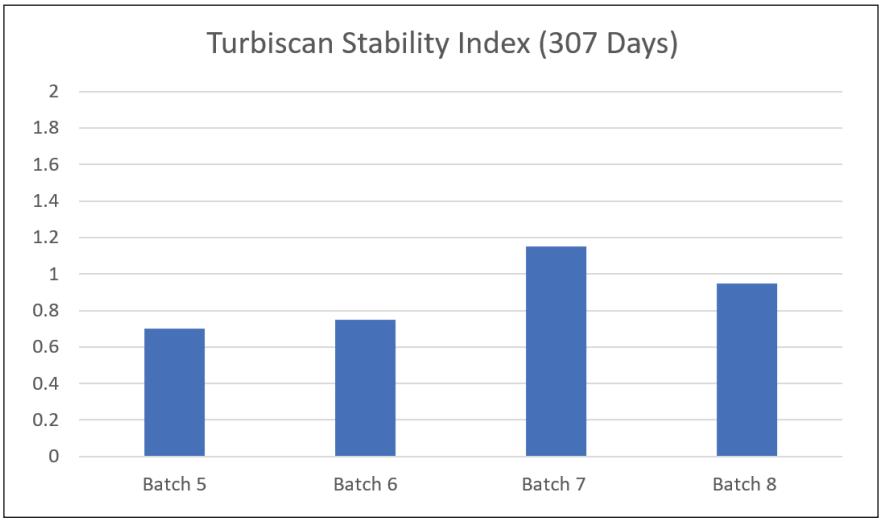


TABLE 5—TSI Rating Key

A+	0-0.5	Visually Excellent	No significant destabilization is observed
A	0.5 to 1	Visually Good	Destabilization is detected but is at a very early stage
B	1 to 3	Visual Pass	The variations detected are higher than the early stage and correspond to the beginning of the destabilization
C	3 to 10	Visual Warning	Important stability destabilization corresponding to large sedimentation/creaming, wide particle size variation, small phase separation
D	>10	Visual Fail	Extreme and important variation and the destabilization most likely visible corresponding to large sedimentation or creaming, phase separation, wide change in the particle size or color

A plot of TSI against time indicates that there is an onset of destabilization of the dispersions at 160 days ambient storage. After 307 days at ambient conditions, all samples demonstrated early-stage destabilization (TSI Class A), considered to be acceptable given that all samples could be easily remixed and incorporated into formulations. No measurement of stabilization in fully formulated paint systems was made and visual observation of paint system indicated no stability or compatibility issues.

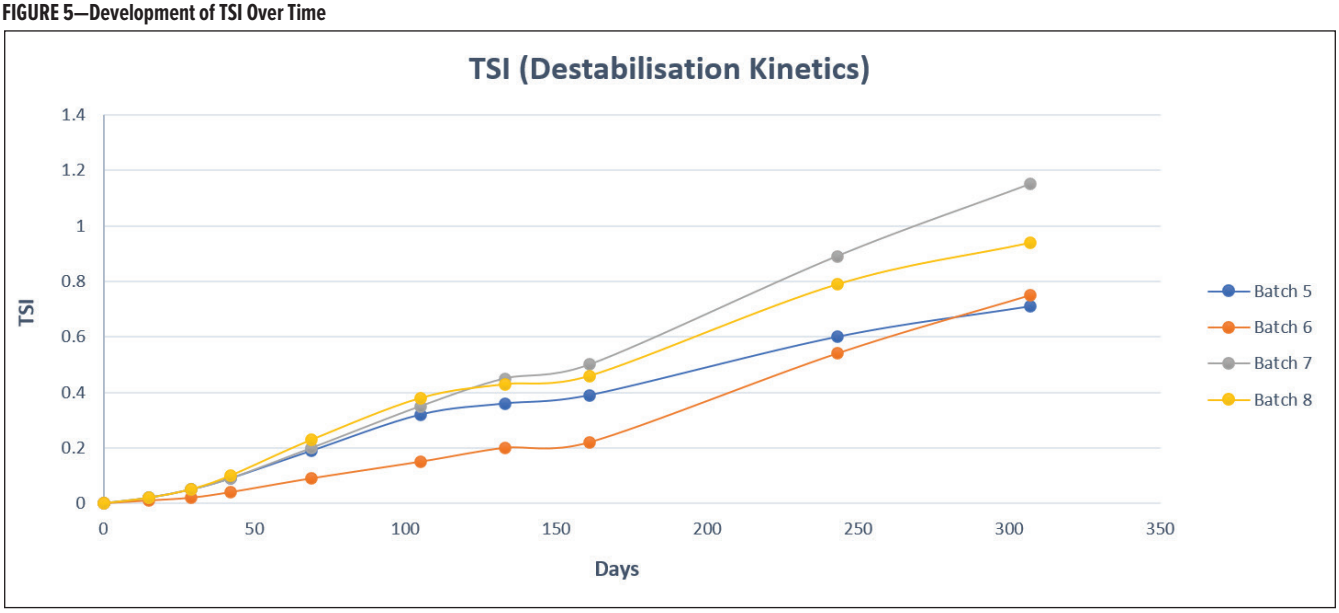
Neutral Salt Spray Testing

Panels were tested to ISO 9227 with neutral salt spray (NSS) and assessed at regular intervals (720, 1440, and 2000 hours) for signs of corrosion creep in accordance with ISO4628. Graphene-modified systems demonstrated reduced creep, and the higher-loaded formulation showing the best performance.

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) has been used extensively to study corrosion of metal substrates and coating performance. EIS can provide additional insights and measurements into the mechanism and onset of corrosion[8,9,10]. The main

FIGURE 5—Development of TSI Over Time



contribution of the coating towards impedance occurs within the lower frequency region, at a frequency close to 0.1 Hz enabling screening in the selection of suitable organic coatings.

Panels were prepared as detailed and initial EIS measurements conducted. Afterward, samples were exposed to NSS and removed at intervals for measurement. All electrochemical measurements were recorded using a Gamry 1000E potentiostat in conjunction with a Gamry ECM8 multiplexer.

It is possible to determine values of water uptake in organic coatings from EIS data. Such coatings can behave as parallel plate dielectric capacitors where the metal substrate acts as one "plate" and the electrolyte acts as the other "plate." At a fixed coating film thickness and measured test area, the capacitance of the coating is dictated by its dielectric constant.

In turn, the dielectric constant of the overall formulated coating is influenced by the dielectric constants [and volume fractions] of the individual coating components (e.g., binder, fillers, and pigments). Most organic coatings have a dielectric constant in the range of 5-10. Water, on the other hand, has a much larger dielectric constant of approximately 80, due to its polar nature. Therefore, an influx of water into the coating will lead to an increase in capacitance, which may then be related to water uptake, as set out in the Brasher and Kingsbury equation

$$X_v = \frac{100.\log C_m(t)/C_m(t=0)}{\log \varepsilon_w}$$

where C_m (t=0) = capacitance at zero time, C_m(t) = capacitance at time t, and ε_w is the dielectric constant of water.

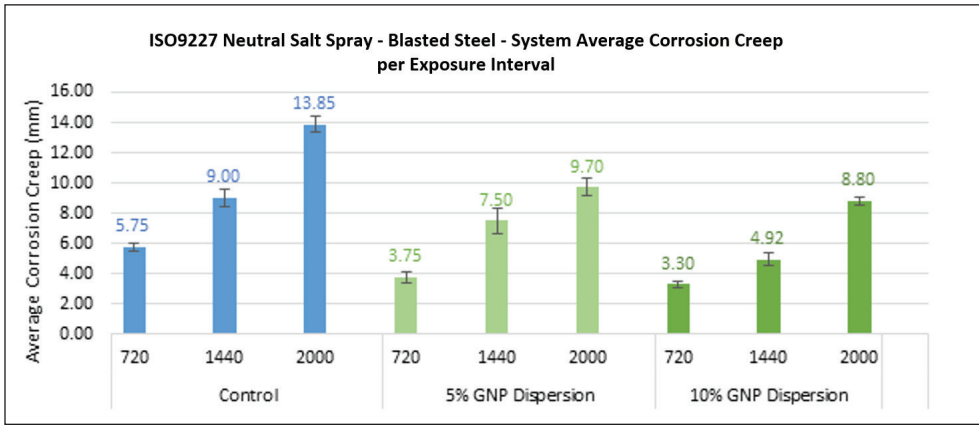
The impedance data, shown for all coatings in *Figure 7* and *Figure 8*, shows improved impedance through graphene incorporation, suggesting both samples possess better barrier properties over the control sample. This is also reflected in the water uptake data shown in *Figure 9*.

DISCUSSION

The barrier properties of coatings are influenced by several factors: hydrophobicity (based on chemical composition and morphology), crosslink density, polarity, and the creation of good wet adhesion through the presence of polar groups which interact with the substrate. The use of platelike pigments in solvent-based systems have been shown to introduce a further factor, that of tortuosity—an increase in the total pathway of water, dissolved oxygen, and electrolytes to the metal substrate. Graphene has been demonstrated to provide efficient and effective barrier properties promoting improved corrosion performance in solvent-based systems.[1]

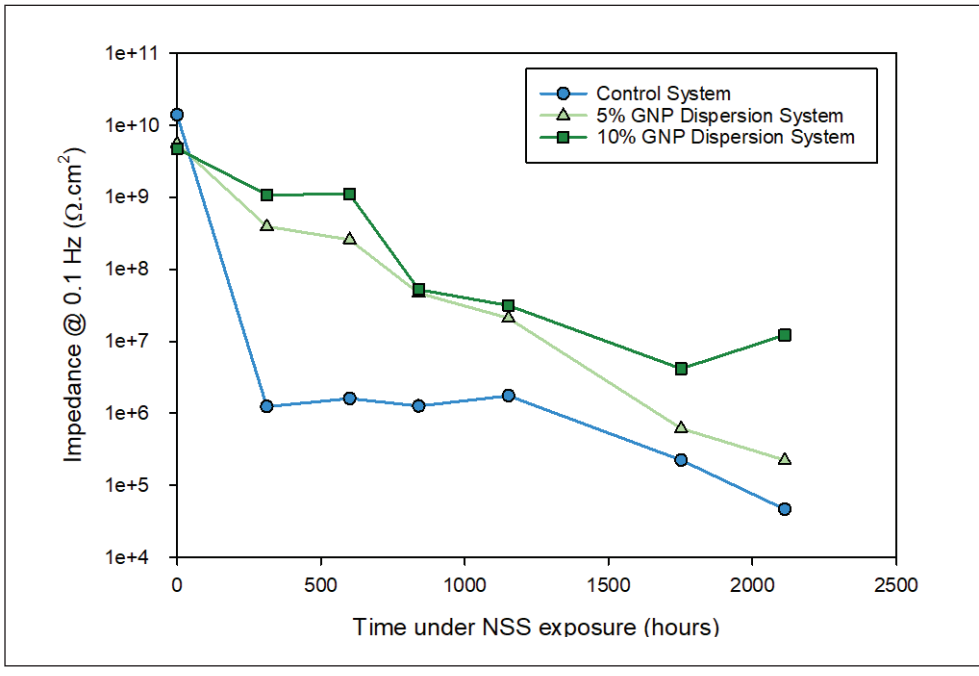
The use of graphene in this waterborne formulation for anticorrosion activity has been evaluated by ISO9227 NSS and EIS. The results shown demonstrated improved corrosion resistance in NSS testing, in comparison to the standard control system up to 2000 hours' exposure. Both graphene loadings show a reduction in average corrosion of 43.1% and 36.5%, respectively, at 2000 hours. EIS testing demonstrated improved retention in impedance and reduction in water vapor uptake over exposure time, suggesting that graphene may function to improve tortuosity as previously demonstrated in solvent-based systems.

FIGURE 6—Average Corrosion Creep on NSS Testing



Samples were measured a minimum of six times across the scribe defect with an equal number of measurement points taken from either side of the midpoint with a spacing of 5 mm between points.

FIGURE 7—Impedance at 0.1 Hz



A key parameter to imparting improved corrosion performance of graphene is achieving good dispersion, so enabling the effective distribution of the graphene nanoplatelets through the film. The authors have developed a range of dispersions that can be easily incorporated into water-based paints and coatings using traditional paint manufacturing methods so enabling application of graphene nanoplatelets in waterborne systems and an improvement in corrosion performance.

CONCLUSION

The use of graphene nanoplatelets, introduced using compatible and stable GNP dispersions, has been shown to improve corrosion resistance. EIS results indicate higher retention of impedance together with reduced water uptake suggesting that the mechanism of action is comparable to that seen in solvent-based systems. This results in significantly improved anticorrosive performance of water-based epoxy coatings. ❊

FIGURE 8—Impedance Data for All Systems Under NSS Exposure Over the Full Frequency Range (Bode plots)

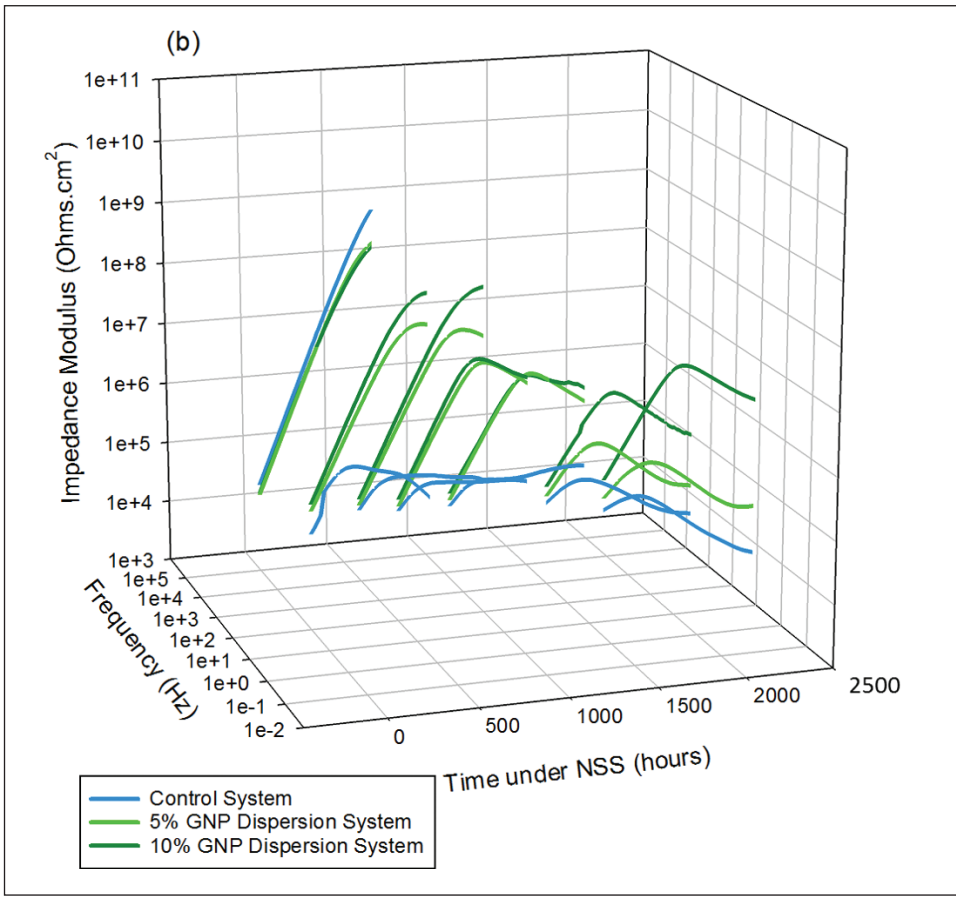
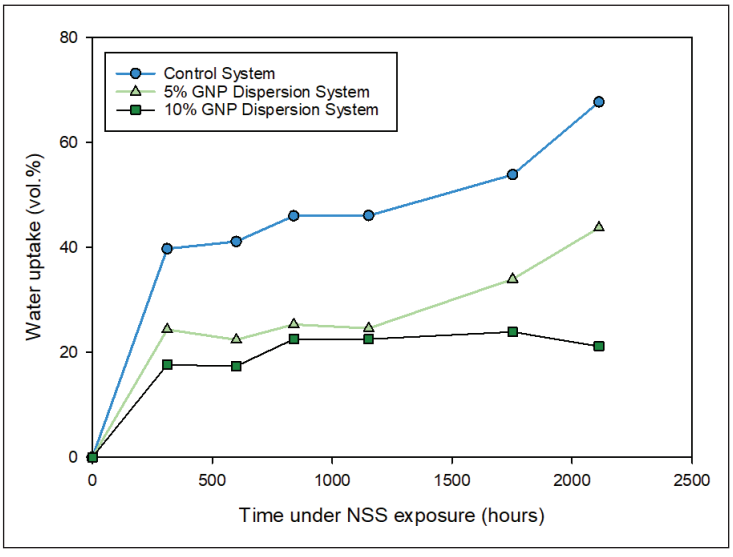


FIGURE 9—Water Uptake vs. *Time Under NSS Exposure*



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