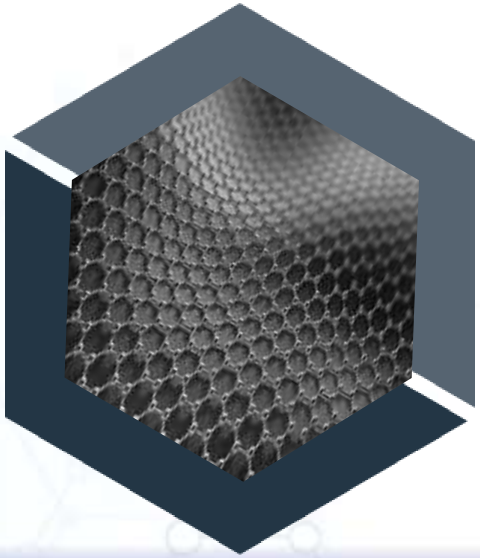
Coatings Trends & Technologies

Industrial Coatings: Use of Graphene Nanoplatelets to Enhance Chemical Resistance of Epoxy Systems

Introduction

- In its purest form, graphene possesses an unsurpassed combination of **electrical**, **mechanical** and **thermal** properties, which gives it the potential to replace existing materials in a wide range of applications and, in the long term, to enable new applications.
- Graphene's unique **two-dimensional** structure in the nanoplatelet form results in very high aspect ratio, high surface area materials which are particularly suited for use as **multi-functional additives** in paints and coatings formulations.



Introduction

Coatings Trends & Technologies

According to Industry ARC (Analytical Research Consulting), The **Global Chemical Resistant Coatings Market** size is forecast to reach **US $8.3 billion** by 2026, after growing at a CAGR of 5% during 2021-2026.

Chemical resistant coatings are designed to protect against the harshest of chemicals.

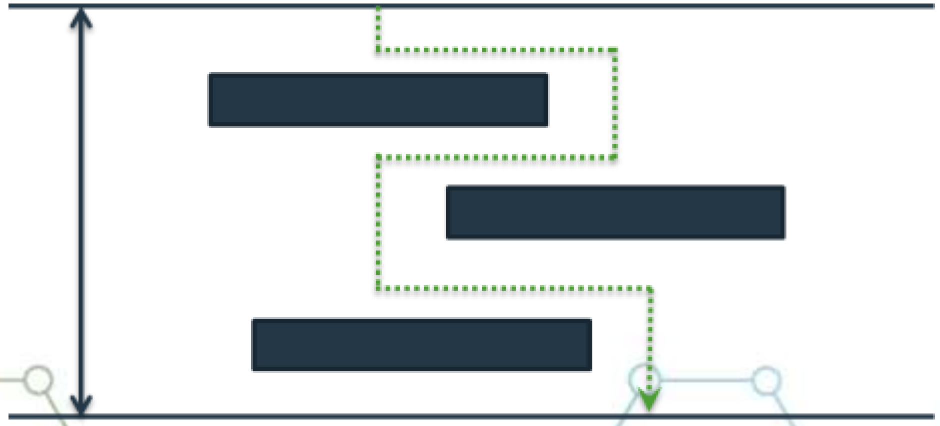
Key trends and applications

- Chemical resistance coatings are a necessity in a variety of applications in infrastructure, wastewater treatment and petrochemical industries.
- Encompassing uses such as layering, varnishing, or flooring applications in wastewater treatment plants, sewer, containment zones, and power plants, among others.
  - Global water consumption rate has been increasing by 100%, every twenty years. The rising scarcity for potable water, coupled with the growing population and increasing water demand, is the major concern that has been driving the demand for the water treatment industry. The growing number of construction of **water treatment plants** has been mainly driving the demand for the chemical resistant coatings.
  - New **manufacturing plants** in the food processing industry are also expected to drive the market demand.
  - Construction of new **power plants** have also been boosting the chemical resistant coatings for flooring in the recent times.

Previous Work

- The main method of protection from GNPs in chemical resistant coatings is as a barrier pigment. Lamellar shaped barrier pigments are known to create a **tortuous pathway** for molecules trying to make their way through the coating.
- As nanomaterials (including GNPs) are much **thinner** than traditional barrier pigments such as glass flake, they have a very high aspect which results in significantly higher tortuosity when compared to traditional barrier pigments.

This is demonstrated using the **Nielsen model** below:



In this case,

	Lateral dimensions (um)	Platelet thickness (um)
GNP	12	0.005
Glass Flake	50	2.8

Total path of a diffusing gas

$d^1 = d + d*L*V_f/2W$

d = coating thickness (80 microns)
L = length of platelet
W = width of a single platelet
V_f = volume fraction of platelets

Tortuosity factor

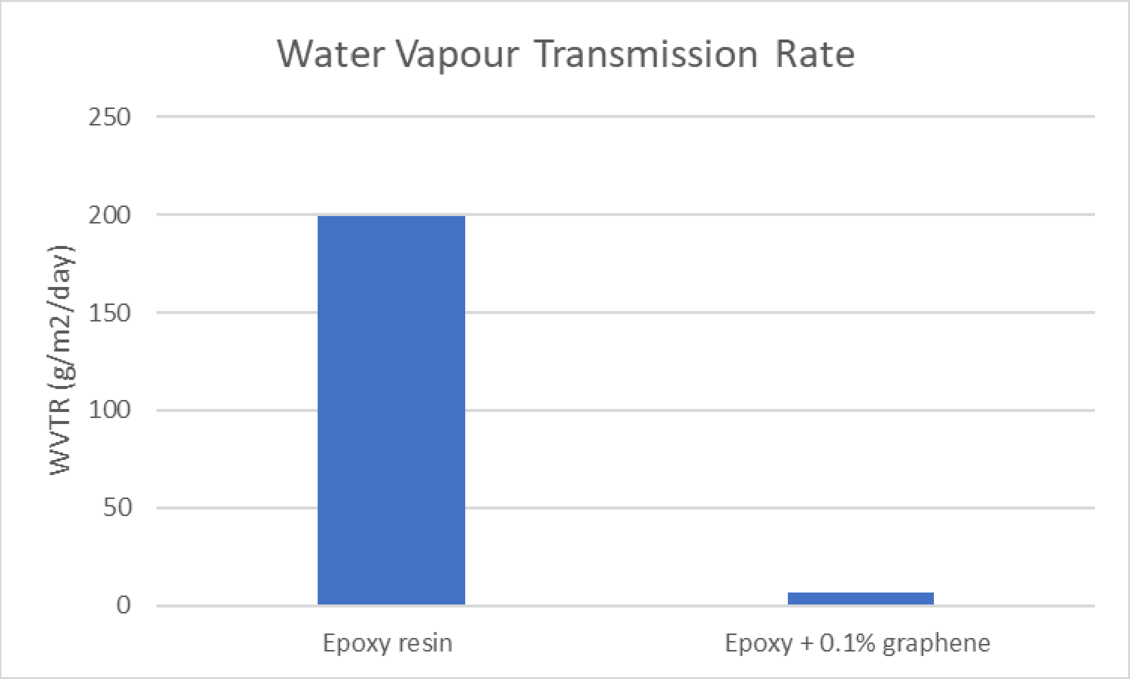
$T = d^1/d$
$= 1 + L*V_f/2W$

		20% Glass Flake	0.5% GNP	1% GNP	2% GNP
d1	Diffusion pathway (µ)	334.72	2017.47	3896.70	7490.66
t	Tortuosity factor	4.18	25.22	48.71	93.63

Previous Work

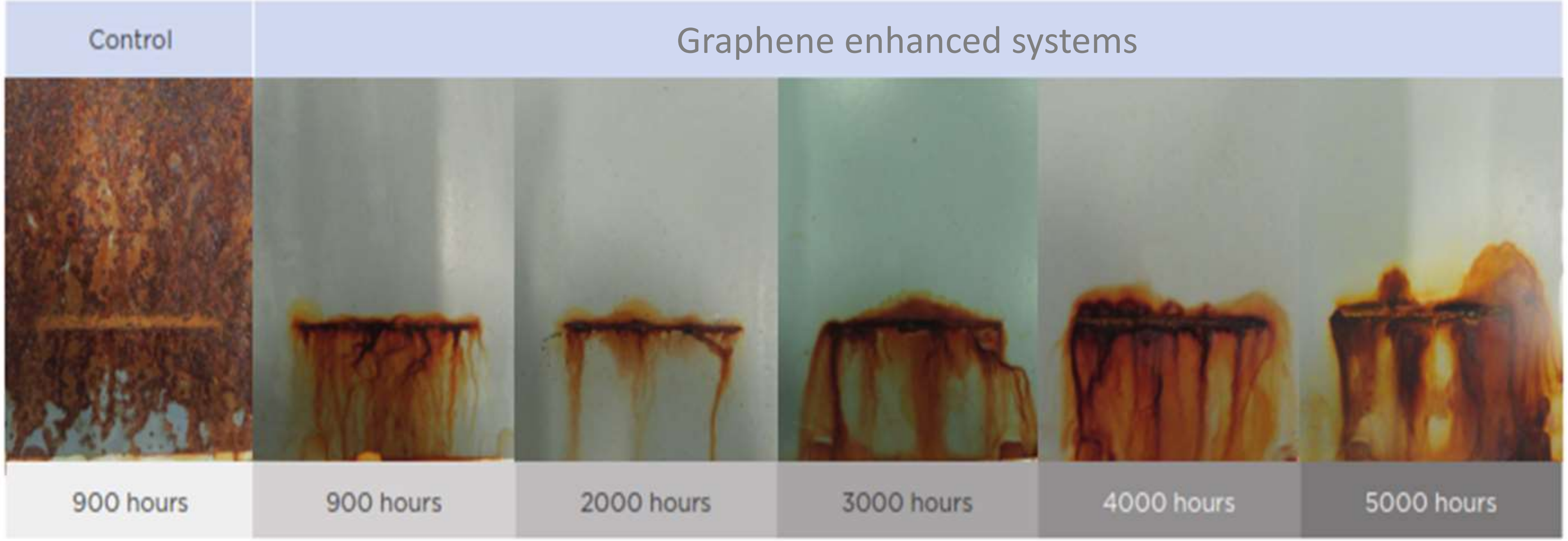
- It has long been theorized that GNPs, when incorporated into an organic coating system or host matrix, provide a highly tortuous pathway which acts to **impede the movement** of corrosive species towards the metal surface.
- One way to effectively demonstrate this, is through **water vapor transmission rate (WVTR)** testing.

The introduction of graphene nanoplatelets resulted in a **greater than 95% reduction** in water vapour transmission rate, indicating barrier type properties.



Previous Work

- Having shown that graphene has good **barrier** properties, further work was carried out to determine whether this can be used to achieve meaningful anticorrosive performance gains in epoxy primers.
- In one series of tests, performance on ASTM G85 prohesion test was **extended** from 1000 to 5000 hours by using graphene in combination with metal free active inhibitors.



Objective

Having demonstrated the benefits of graphene as a **barrier** material that can impart corrosion resistance properties into coatings, further work was carried out to investigate whether the same barrier mechanism could be used to improve the **chemical resistance** of epoxy coatings.

EXPERIMENTAL

Experimental

Coatings Tested

- Testing was carried out in a liquid epoxy resin with an epoxy equivalent weight of 190g/eq, cured with a cycloaliphatic amine at a stoichiometry of 85%.
- System was diluted to 60% solids by weight using a 3:1 blend of xylene: butanol.
- All testing was carried out in clear coats.
- Graphene nanoplatelets were introduced at loadings of 0.5, 1 and 2% loadings by weight and tested against glass flake at a loading of 20%.

Panel Preparation

- Panels were applied by drawdown applicator, achieving a DFT range of 80 +/-10 microns.
- All systems were allowed to cure for 7 days under ambient lab conditions before testing.

Experimental

- Panels were half immersed in different chemical media for a period of **28 days**.
- The media selected were chosen to be **representative** of weak and strong acids and bases, as well as organic solvents.

	Immersion Media
Acids	10% Lactic Acid
	10% Suphuric Acid
Bases	10% Sodium Hypochlorite
	50% Sodium Hydroxide
Organic solvent	Methyl Ethyl Ketone
Other	De-Ionized Water

RESULTS

Resistance to Acids

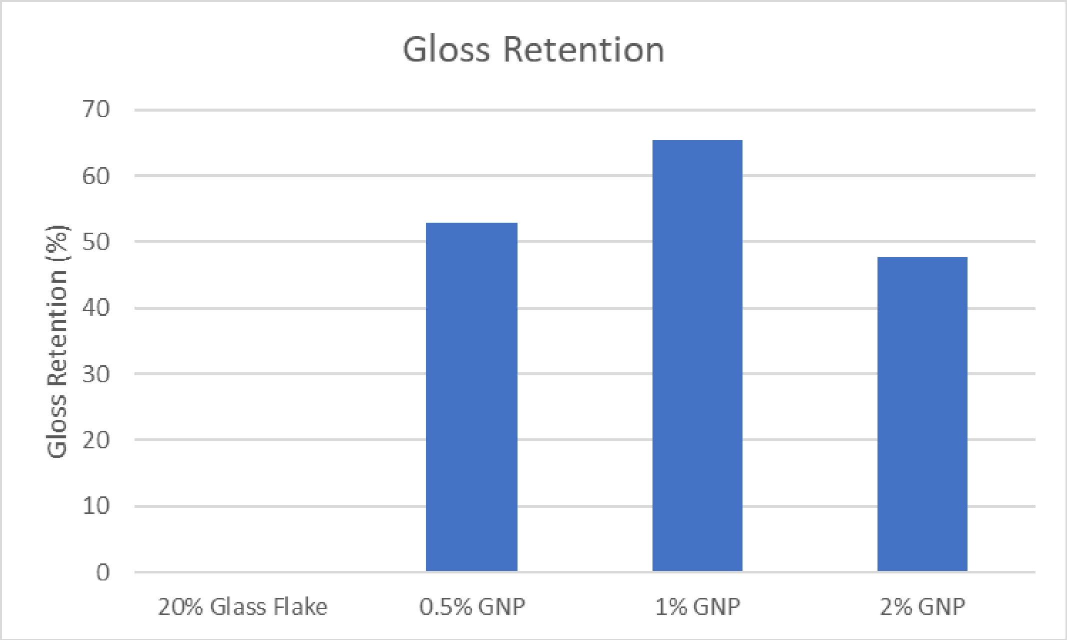
20% Glass Flake

0.5% GNP

1% GNP

2% A-GNP

28 Day Immersion in 10% Sulphuric Acid



Visual Assessment

- GNP modified systems outperforming glass flake, with blistering only being observed on glass flake

Gloss Retention

- No gloss measurements on glass flake due to high degree of blistering.

Resistance to Acids

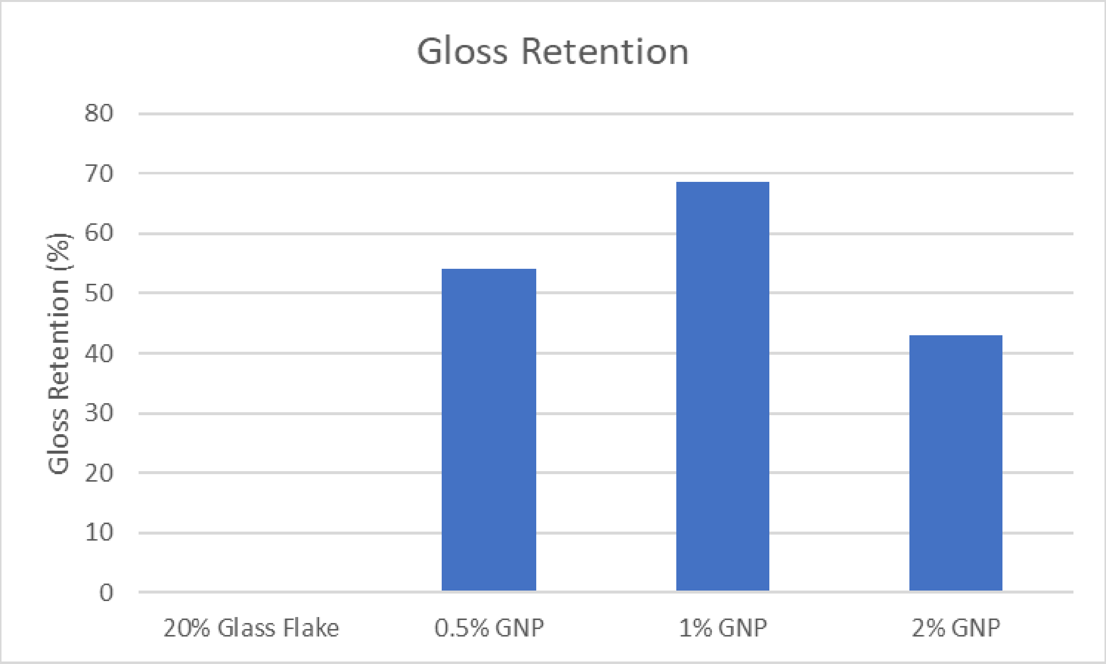
20% Glass Flake

0.5% GNP

1% GNP

2% A-GNP

28 Day Immersion in Lactic Acid



Visual Assessment

- Glass Flake immersed area showed discolouration

Gloss Retention

- No gloss measurements could be taken for glass flake due to surface roughening.

Resistance to Bases

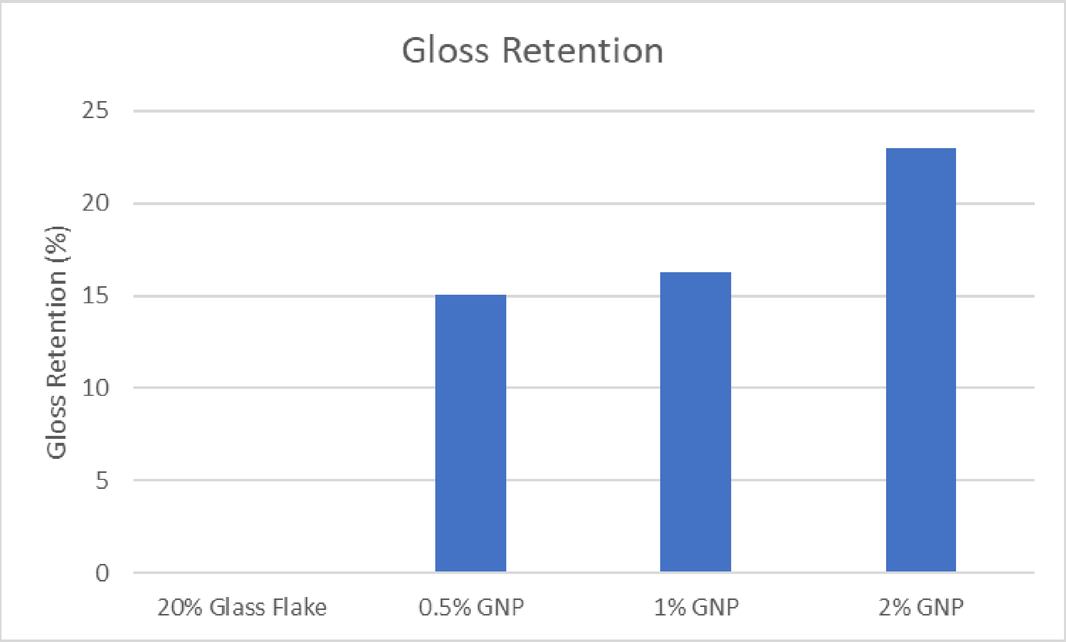
20% Glass Flake

0.5% A-GNP

1% A-GNP

2% A-GNP

28 Day Immersion in 10% Sodium Hypochlorite



Visual Assessment

- Degradation of glass flake coating and rusting of the substrate after 28 days immersion in sodium hypochlorite.
- GNP coatings showed whitening of the surface and no other defects.

Gloss Retention

- Gloss measurements could not be taken for glass flake due to coating degradation.
- For the graphene enhanced systems, the higher the loading of graphene, the better the gloss retention.

Resistance to Bases

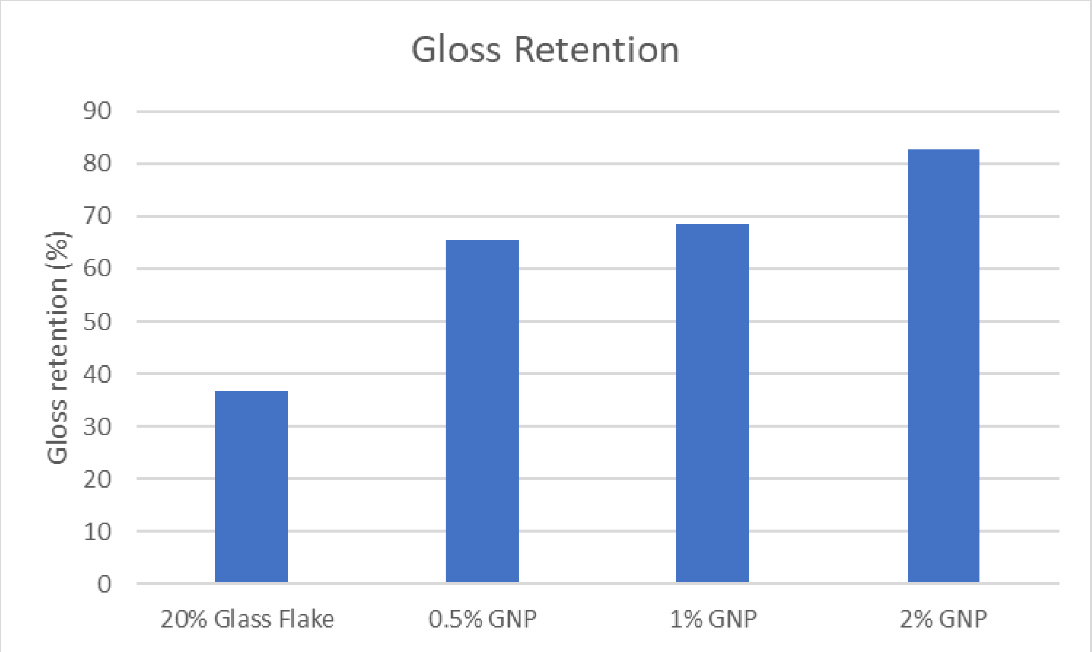
20% Glass Flake

0.5% A-GNP

1% A-GNP

2% A-GNP

28 Day Immersion in 10% Sodium Hydroxide



Visual Assessment

- No blistering or visible discolouration for any of the panels

Gloss Retention

- Higher gloss retention achieved with GNP modified systems
- The higher the loading of graphene, the better the gloss retention.

Resistance to Organic Solvents

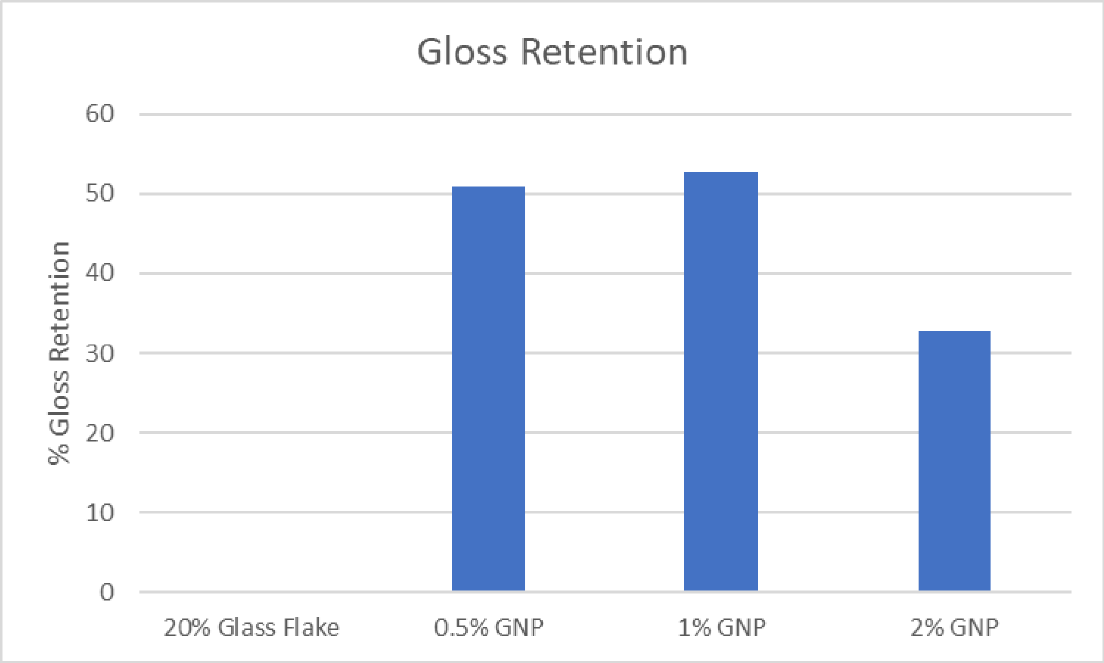
20% Glass Flake

0.5% A-GNP

1% A-GNP

2% A-GNP

28 Day Immersion in MEK



Visual Assessment

- Surface roughening of 20% glass flake coating
- No visible changes of the graphene modified systems

Gloss Retention

- No gloss measurements could be measured on the glass flake system due to the coating defects
- The lower loadings of graphene performed better than the highest loaded sample.

Resistance to Deionised Water

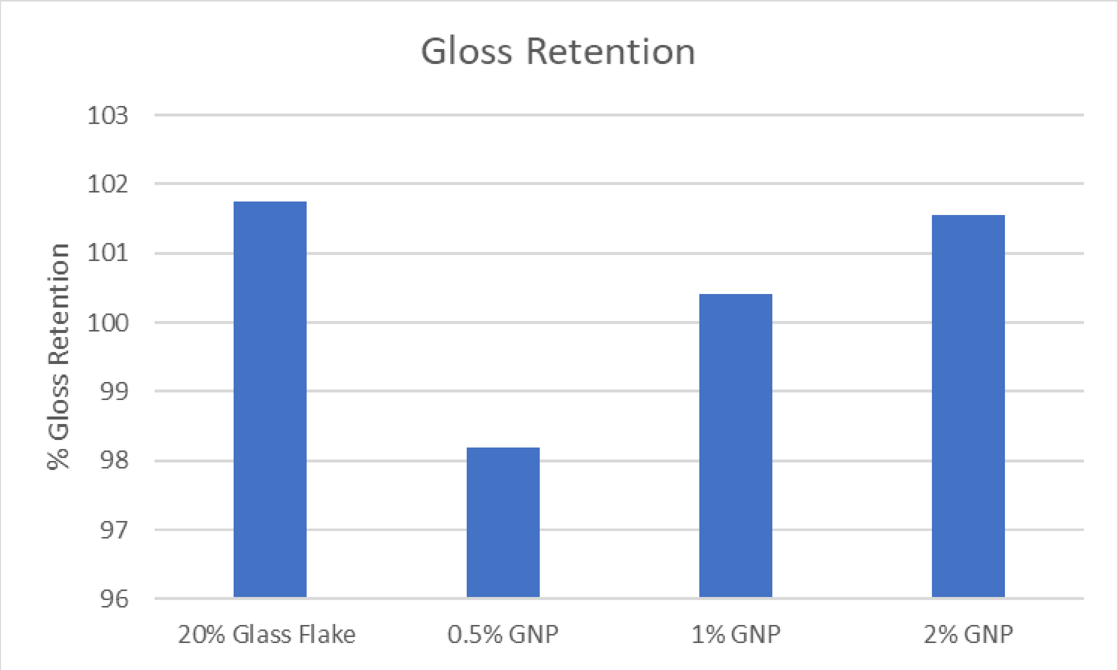
20% Glass Flake

0.5% A-GNP

1% A-GNP

2% A-GNP

28 Day Immersion in Deionised Water



Visual Assessment

- Discolouration on 20% glass flake coating. No defects observed with the GNP modified coatings.

Gloss Retention

- Glass flake gave the highest level of gloss retention. Closely followed by the highest loading of graphene.
- All systems showed a gloss retention greater than 97%.

SUMMARY

Immersion Media (28 Days @ 23°C)		Vs. 20% Glass Flake		
		GNP Loading		
		0.5%	1%	2%
Xylene	Blistering	—	—	—
	Gloss Retention	▲	▲	▲
Butyl Cellosolve	Blistering	—	—	—
	Gloss Retention	▼	▼	▼
MEK	Blistering	▲	▲	▲
	Gloss Retention	▲	▲	▲
10% Lactic Acid	Blistering	—	—	—
	Gloss Retention	▲	▲	▲
10% Sulphuric Acid	Blistering	▲	▲	▲
	Gloss Retention	▲	▲	▲
50% Sodium Hydroxide	Blistering	—	—	—
	Gloss Retention	▲	▲	▲
10% Sodium Hypochlorite	Blistering	—	—	—
	Gloss Retention	▲	▲	▲
Deionised Water	Blistering	—	—	—
	Gloss Retention	—	—	—

▲ Better performance ▼ Worse performance — Equal performance

SUMMARY

- Graphene has previously been shown to have good **barrier properties**; which have been successfully used to improve the **corrosion resistance** of coatings.
- In this work graphene enhanced epoxy coatings were tested for **chemical resistance** to a range of acids, bases, organic solvents and deionized water, over a period of 28 days.
- Performance of the graphene enhanced systems was compared to glass flake, loaded at 20%.
- In 4 of the 5 systems reported, glass flake showed defects such as blistering, surface roughening and rusting while none of the GNP modified systems showed such surface defects.
- In most cases, the GNP modified systems also showed **superior gloss retention** attributes.
- The superior properties of graphene enhanced systems are likely due to the **increased tortuosity** that comes with using very thin nanoplatelets compared to thicker glass flake platelets.

FURTHER WORK

- Epoxy resins are frequently used in protective coating systems as they offer **good resistance** to corrosion and chemical attack.
- There are **several application areas** where improved chemical resistance can prove advantageous, such as marine tank linings and floor coatings; on substrates varying from steel to concrete and wood.
- The authors plan to carry out further work in fully formulated coating systems, that will further demonstrate the benefits of graphene in the above named applications.
- Furthermore, the authors will also explore if additional benefits can be gained from the low loadings of graphene in areas such as mechanical performance.

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Questions?

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