

# Graphene – Epoxy Composites for Anti-Corrosion Coatings

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## ABSTRACT

The use of epoxy (EP) coatings for the protection of steel infrastructure from corrosion is a dominant technology in modern industrial settings. Improvement of this technology by compounding with graphene materials is explored. Composite coatings are produced on steel substrates using graphite nanoplatelets (GNP), more exfoliated graphene materials (MEG), and graphene oxide (GO). The anti-corrosion (AC) performance of the coatings is evaluated by salt-fog corrosion (SFC) testing and electrochemical (EC) methods. GO is found to be an excellent candidate as an AC barrier filler in EP coatings by both SFC and EC testing, clearly outperforming the neat EP. MEG also shows potential as an AC filler by the SFC tests, but performed poorly in the EC tests, possibly due to processing issues at the concentration investigated. GNP is found to show relatively less benefit as an AC filler in EP, compared with the more exfoliated GO and MEG fillers.

**Keywords:** anti-corrosion, epoxy, graphene, composite, coating

## 1. INTRODUCTION

It is important to protect steel infrastructure, such as pipelines, from environmental corrosion. The primary method for this protection is by utilizing coatings, especially epoxy (EP) coatings [1-3]. In recent years graphene has shown a great deal of promise as a candidate for barrier applications, including anti-corrosion (AC) coatings. For example, reduced graphene oxide laminate films produced by the chemical reduction of graphene oxide are found to provide excellent barriers to strong chemicals and salt solutions [4]. A family of new graphenic materials is being developed from the top-down exfoliation of natural graphite, including graphite nanoplatelets (GNP), more exfoliated graphene materials (MEG), and graphene oxide (GO). These materials vary in their properties, with lateral dimensions, the degree of exfoliation, oxygen content, and cost being among the most significant differences, and are suitable for processing with polymers into nanocomposite coatings.

In this work, we explore the viability of processing these materials with EP for application as AC coatings on steel substrates. The AC performance is evaluated by salt-fog (SFC) and electrochemical (EC) corrosion testing. The graphenic materials chosen for these studies show desirable technical characteristics (e.g. homogeneity, high aspect ratios, etc.), and are low-cost and commercially available.

For GNP / EP composites, we previously found an excellent resistance to 1 M HCl aqueous solution over several days in EC testing, as well as a strong resistance to a standard SFC test environment [1]. For both test environments, an improvement in AC performance was seen with a trend towards higher GNP concentrations (above ~1%). The SFC testing further suggested that increasing the lateral dimensions of the GNP materials leads to better improvements in AC performance. A comparison was made with similar published studies [5-7] and it was determined that processing conditions can have a marked effect on the quality of the films and hence the AC test results observed [1]. Here, we report on the further testing of these trends with an expanded concentration range, as well as a comparison with MEG and GO materials.

## 2. MATERIALS AND METHODS

The general material processing procedures used in this study have been described in detail previously [1]. Briefly, the graphenic materials are solution processed into 50  $\mu\text{m}$  nanocomposite EP coatings on steel substrates. The graphenic materials used in this study are GNPs (Angstrom Materials, N006-P, Polar Graphene Powder), MEGs (Angstrom Materials, N002-PDR, Few Layer Graphene Powder), and GO (Graphenea, 2.5 wt% GO aqueous slurry). The GNPs and MEGs are processed as described previously [1], except for, as MEG has a high specific surface area, methylene chloride is added to facilitate the dispersion and blending at higher MEG concentrations ( $\geq 1\%$ ). This mixture is then blended with the curing agent (5 min.), sonicated until a homogenous dispersion is obtained (15 min.), mixed with the EP resin, and heated to 50  $^{\circ}\text{C}$  (5 min.) to evaporate the solvent. The composite is

cooled to room temperature before being cast onto the steel substrates.

The GO is processed after a solvent exchange from water to ethanol and then to acetone following multiple centrifugation steps (3x, 5000 rpm, 10 min) to remove any traces of water, as previously described in the literature [7]. The GO in acetone is then processed similarly to the MEG with methylene chloride slurries to produce a solvent-free composite. The coatings are deposited onto the steel substrates by spin-coating (40 s at 700 rpm followed by 10 s at 1000 rpm) and then cured. SFC and EC testing is performed as described previously [1]. The edges and back side of the steel substrates (72.5 mm diameter) are protected with a thick layer of EP for the SFC test. Scanning electron microscope (SEM) imaging of the graphene materials is performed using a Hitachi S-4800 instrument operated at 5-15 kV.

### 3. RESULTS AND DISCUSSION

#### 3.1 Material Characterization

SEM images of the graphene materials used to make the composites for these studies are shown in Figure 1 (the GO slurry is dried in air at 100 °C prior to imaging to remove the water). The GNPs show a rigid, platelet morphology with typical lateral dimensions on the order of 10 μm. The MEGs show a “crumpled tissue” morphology with fine features consistent with a more exfoliated material and typical lateral dimensions on the order of 20 μm. The dried GO shows a continuous sheet morphology with fine features indicating a high degree of exfoliation. The drying process appears to produce a dense, conformal coating on the substrate.

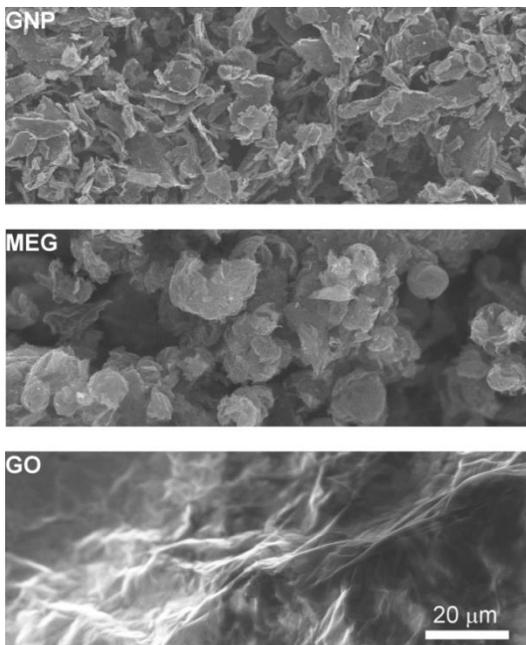


Figure 1: SEM images.

#### 3.2 Salt-Fog Testing

SFC testing is performed on the composite coatings for 302 h (32 samples, including duplicates of neat EP and duplicates of each of the graphene materials (GNP, MEG, GO) at 0.33, 0.67, 1.0, 1.5, and 2.0 wt% in EP). Different types of corrosion are observed including isolated rust dots at the interface between the coating and the steel substrate in the interior of the sample and at the boundary between the coating and the edge protection (see Figure 2). With longer exposures, some samples show continuous areas of rust and signs of coating delamination. To compare the effects of the different graphene formulations, subsequent analysis of the corrosion is limited to the corrosion at the interior of the coating, which does not appear to be related to the boundary with the edge protection or delamination.

Visual scores are assigned to the samples under test as a function of exposure time to the SFC environment [1], with typical results shown in Figure 2. It is found that, in general, the MEG coatings hold up extremely well at all concentrations and easily outperform the neat EP. The GO performs better than the neat EP, in general, but with some outliers and scatter in the data possibly caused by pinholes in the coatings that are generated during the solvent drying process used with the GO processing. The GNP material performances are found to be comparable (or slightly better) to that of the neat EP, as we previously observed [1]. Overall the material performance is found to follow the trend: MEG > GO > GNP > EP. No clear trends with concentration are found in these data for any of the graphene materials.

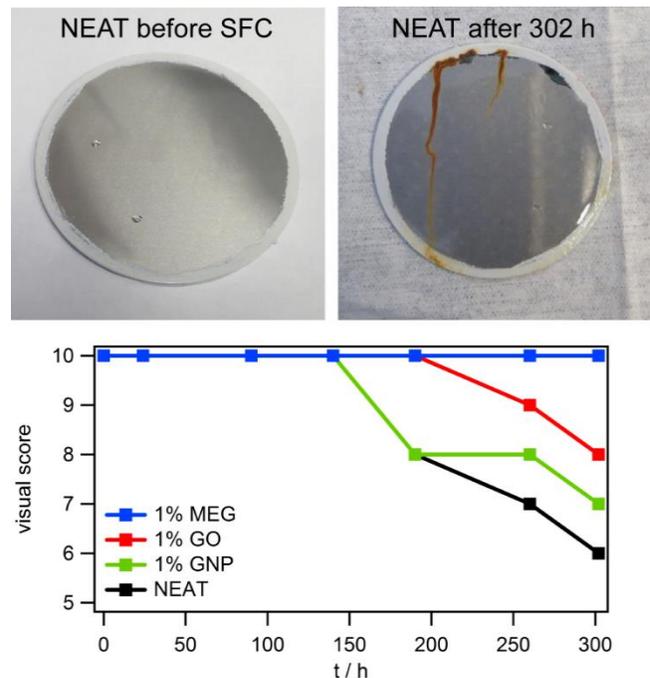


Figure 2: Typical SFC test results.

### 3.3 Electrochemical Testing

Coating capacitances and resistances are extracted from electrochemical impedance spectra taken from the composite coatings as a function of soak time in 1 M HCl, following our previously described methodology [1]. Neat EP and 1% composite coatings are initially considered. Comparison of the coating capacitances as a function of soak time suggests that the 1% GO coating is showing better AC performance than the neat EP coating and the 1% GNP coating is performing worse (see Figure 3(a)). Maintaining a lower capacitance for a longer soak time indicates less penetration of the corrosive solution into the coating and hence better AC performance.

Comparison of the resistance evolution (Figure 3(b)) suggests that both the GO and GNP composite coatings are showing better AC performance than the neat EP (less current); however, the resistance is a less precise parameter to monitor due to the solution resistance in series with the coating resistance. The 1% MEG coating is found to show an anomalous behaviour that did not fit well to the circuit model (data not shown), likely due to the problems with dispersing the MEG at this concentration. Further testing is underway to investigate how concentration affects the MEG composite coating performance.

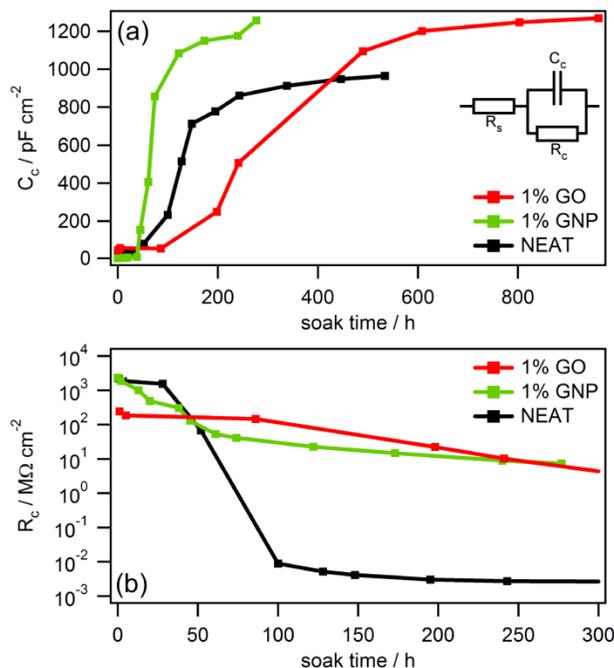


Figure 3: Electrochemical results.

### 3.4 Discussion

A comparison of the SFC test results with the EC ones suggests that the GO is an excellent candidate for an AC barrier filler in EP coatings. In both test environments, 1% GO composite coatings clearly outperformed the neat EP coatings. The as received GO has a high degree of

exfoliation and large lateral dimensions (high aspect ratio) making it an ideal material for barrier applications. The GO also has functional groups that may interact favourably with the EP, leading to a high quality dispersion. The GO comes as an aqueous slurry, which eliminates problems with restacking of the layers and facilitates good dispersion in the EP matrix. Any issues with elimination of the water (which would interfere with the EP curing process) appear to be manageable.

The MEG composite coatings at 1% show an excellent AC performance in the SFC test, even outperforming the GO composites. However, this favourable performance is not seen in the EC test results. The as received MEG, like the GO, also has a high degree of exfoliation and a high aspect ratio but comes as a dry powder. When processed with the EP at concentrations of around 1% or higher, this high surface area leads to processing issues that require the use of solvents to overcome. These processing issues may be source of the discrepancy between the AC performances determined by the SFC and EC experiments. Further EC experiments are underway at lower MEG concentrations to investigate these issues further.

For both the SFC and EC tests, the 1% GNP composite coatings did not show significant relative gains in AC performance over the neat EP coatings, compared to GO and MEG. The as received GNP material is much less exfoliated than either the GO or MEG materials, showing many of the same properties as bulk graphite [1]. Clearly, these lower aspect ratios do not lead to the same performance gains seen with the high aspect ratio fillers. The GNPs are also more rigid than either the MEG or GO and may not conform well inside the EP coating during processing, leading to issues with cracks and pinholes. Even if the GNP is providing some barrier effects, these cracks and pinholes may be counteracting any gains being provided by the barrier. Overall, the MEG and GO materials appear to show the greater promise for further development as AC composite fillers with EP coatings.

## 4. CONCLUSION

In summary, graphene – EP composite coatings are produced on steel substrates using GNP, MEG, and GO. The AC performance of the coatings is evaluated by SFC testing and EC methods. GO is found to be an excellent candidate as an AC barrier filler in EP coatings by both SFC and EC testing, clearly outperforming the neat EP. MEG also shows potential as an AC filler by the SFC tests, but performed poorly in the EC tests, possibly due to processing issues at the concentration investigated. GNP is found to show less benefit than the MEG or GO as an AC filler in EP. Further EC testing is underway at different concentrations to expand on these results for both the GO and MEG composite coatings.

## ACKNOWLEDGEMENTS

Funding for this work was provided by National Research Council Canada, Nanotechnology Research Centre (formerly National Institute for Nanotechnology).

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