TECHNICAL APPLICATION NOTE

Conductivity

Contents

1. **Introduction to AGM**

Applied Graphene Materials UK Ltd (AGM) manufacture graphene nanoplatelets using a proprietary and patented process developed at Durham University in the UK.

Applied Graphene Materials UK Ltd have developed significant in-house knowledge on the behaviour and performance of graphene modified coating formulations. These guidance notes are designed to provide formulation insights to assist development scientists achieve a technological appreciation of the novel technology.

The first part of the note provides background on conductive coatings and the second describes the behaviour of graphene on conductivity when dispersed into resins, solvents and fully formulated pigment paints.

2. **Introduction to Conductive Coatings**

Graphene, as a multifunctional nano material, has attracted attention from the coatings industry in recent years, primarily due to its barrier, mechanical, thermal and electrical properties.

In its purest form, graphene is a single layer of carbon atoms, arranged in a hexagonal lattice. Graphene nanoplatelets (GNPs) consist of several layers of graphene sheets and offers` a manageable route to the commercialisation of graphene-loaded coatings. Applied Graphene Materials (AGM) has developed a synthetic route for the manufacture of graphene nanoplatelets plus the technology to deliver stable graphene dispersions to the coatings market.

It has been theorised that the characteristic two-dimensional structure and the presence of delocalised electrons contributes to the conductivity of graphene. AGM have worked with independent industry experts to evaluate their synthesised graphene nanoplatelets as a powder dispersed in epoxy systems in order to demonstrate the level of conductivity against basic epoxy resin.

As a first step, the conductivity of AGM's graphene nanoplatelets was benchmarked. Addition of loadings as low as 0.5% by weight of graphene nanoplatelets to epoxy resin was found to improve the resulting conductivity of the resin system, achieving bulk resistivity levels as low as 10^3 Ohm.m. The potential to replace conventional raw materials with graphene at much lower loadings has therefore sparked significant interest.

In order to achieve the reported conductivity levels in real end products, AGM has developed and optimised a range of stabilised water, solvent and resin based dispersions which can improve the conductivity of a coating. The impact of particle size and loading level in AGM graphene dispersions was also investigated.

This technical application paper presents results of conductivity testing in graphene enhanced epoxy coatings, solvents and fully formulated pigmented paint systems whilst also benchmarking GNPs against a commercially available alternative conductive carbon black. The importance of achieving a good quality dispersion without compromising on platelet dimensions will also be reviewed.

2.1. Background on Conductivity in Coatings

2.1.1. Definition of Electro Static Discharge (ESD) Materials

**Definition of Surface Resistivity and Volume Resistivity**

Surface Resistivity is a measurement of the resistivity of a material along the plane or surface of the sheet. It is a useful measurement when measuring a thin film of material with a uniform thickness because it is independent of the material thickness, and can be measured across a range of (thin) thicknesses. Sheet resistance is expressed as ohms/sq, spoken as "ohms-per-square". This unit is only used for sheet resistance because it is dimensionally the same as an ohm.

The following terms are used interchangeably: **Sheet Resistivity = Sheet Resistance = Surface Resistivity = Surface Resistance**

Volume Resistivity, is a measurement of the resistivity of a material perpendicular to the plane. As such, we can multiply the sheet resistance by the thickness of the material (in centimetres) to give a volume resistivity in "ohms-cm" or ohms-centimetres. Likewise, the Volume Resistivity divided by the thickness in centimetres equals the surface resistivity.

The following terms are used interchangeably in literature: - **Volume Resistivity = Volume Resistance = Bulk Resistivity = Bulk Resistance**

The difference between Surface (or Sheet) Resistivity and Volume Resistivity is shown pictorially below.
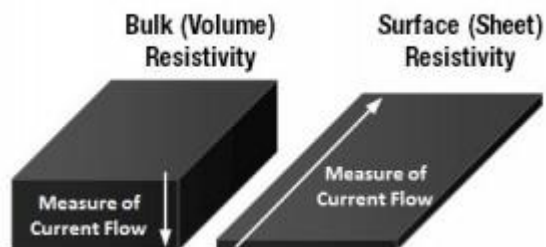
Volume Resistivity vs. Volume Conductivity

Volume resistivity (bulk resistivity) is a measure of the resistivity across a defined thickness. Resistivity is the inverse of conductivity, since volume resistivity is measured in Ohms-cm, or spoken as "ohms-centimetre", volume conductivity is one-over-ohm-cm ($1/\Omega$-cm) and is measured in S/cm, or spoken as "Siemen per centimetre".

2.1.2. ESD Materials Categories

The ESD material categories chart below is shown by category for surface resistivity range (ohm/square) against material/application area.

Metals	Carbon Powders & Fibres			Shielding Composites			Conductive Composites			
10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10	10^{2}	10^{3}	10^{4}	10^{5}	10^{6}

Static Dissipative Composites			Anti-static Composites			Base Polymers			
10^{7}	10^{8}	10^{9}	10^{10}	10^{11}	10^{12}	10^{13}	10^{14}	10^{15}	10^{16}

Materials for protection and prevention of Electrostatic Discharge (ESD) can be categorised into three distinct groups-separated by their ranges of conductivity to electrical charges.

Anti-Static-Resistivity generally between 10^9 and 10^{12} ohms per square. Initial electrostatic charges are supressed. May be surface resistive, surface coated or fixed throughout.

Static-Dissipative-Resistivity generally between 10^6 and 10^9 ohms per square. Low or no initial charges-prevents discharge to and from human contact. May be either surface coated or filled throughout.

Conductive-Resistivity generally between 10^2 and 10^6 ohms per square. No initial charges, provides path for charge to bleed off. Typically containing carbon particle or carbon fibre.

Ref (www.pac.on/art-esd-resistivity)

3. Comparison of A-GNP35 with Ketjen Black

#### 3.1. In-house Comparison of A-GNP35 with Ketjen Black

Ketjen Black EC-600JD is an AkzoNobel product that is marketed as a high surface area carbon black suitable for electro-conductive and antistatic applications. Lower loadings of EC-600JD are typically required to achieve similar levels of conductivity to "conventional" carbon blacks.

3.2. Testing

Testing was carried out at AGM to understand the conductivity of A-GNP35 compared to Ketjen Black at equivalent loading levels. Both A-GNP35 and Ketjen Black were added to an epoxy (EEW=190g/eq) and dispersed at 1.1% w/w loading using a Thinky Mixer. The Epoxy was cured at room temperature using Epikure 3234 hardener and left to harden for two days.

Bulk and Surface Resistivity measurements were made based upon the ASTM D257 standard.

Surface Resistivity
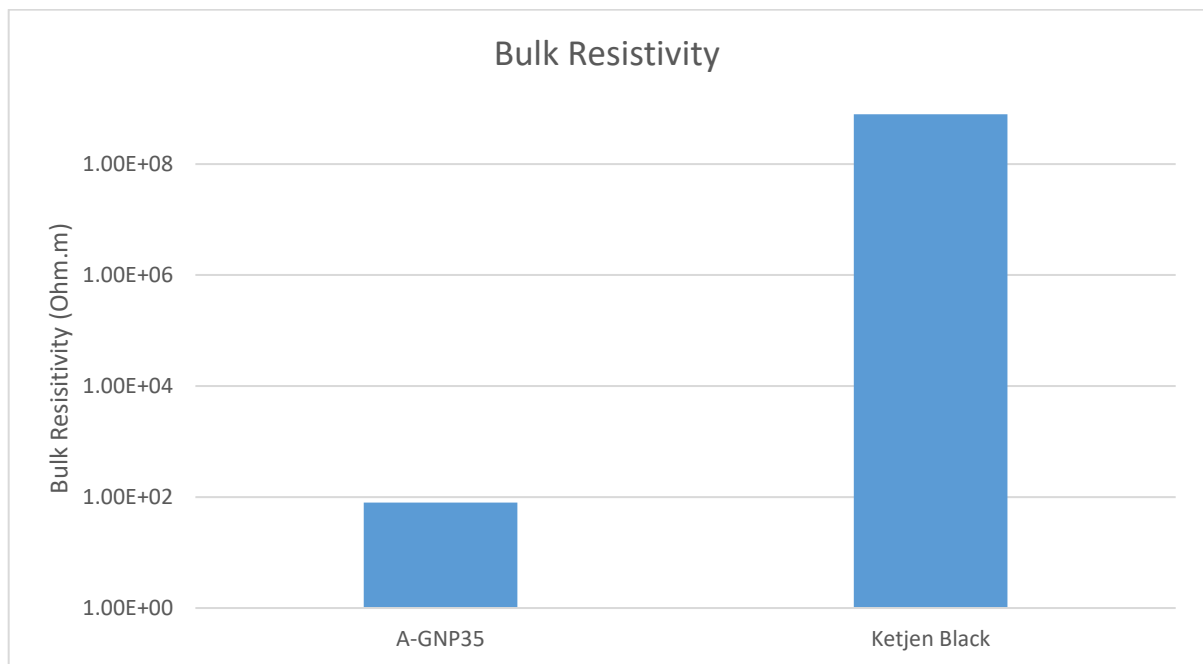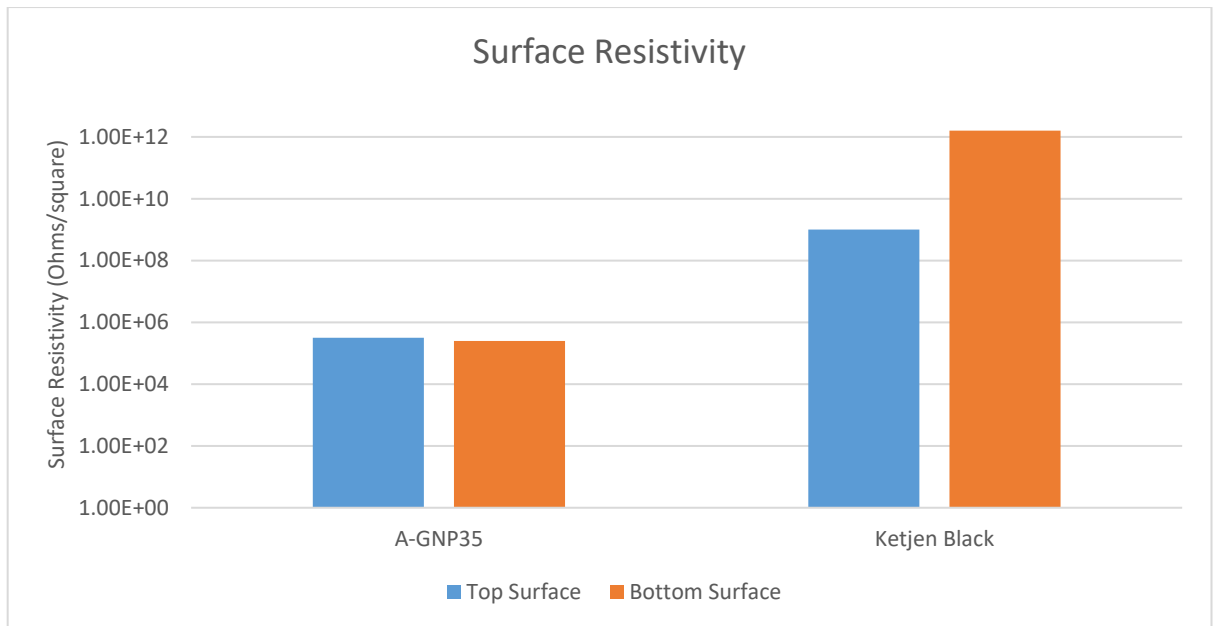
The relationship between viscosity and conductivity was also investigated at various loading levels of A-GNP35 and Ketjen Black.

	Viscosity (Pa.s @ 10 S^{-1})	Surface Resistivity –Top (Ohms/Square)
Neat Epoxy	0.56	2.12E+12
1% Ketjen Black	8.27	2.50E+08
2.5% Ketjen Black	24.33	3.78E+06
5% Ketjen Black	101.30	3.84E+04
0.2% A-GNP35	4.32	6.40E+11
0.4% A-GNP35	15.92	2.52E+11
0.6% A-GNP35	19.48	1.07E+07
0.8% A-GNP35	52.99	2.54E+06
1.0% A-GNP35	85.87	3.71E+05

Ketjen Black Surface Resistivity & Viscosity

A-GNP35 Surface Resistivity & Viscosity
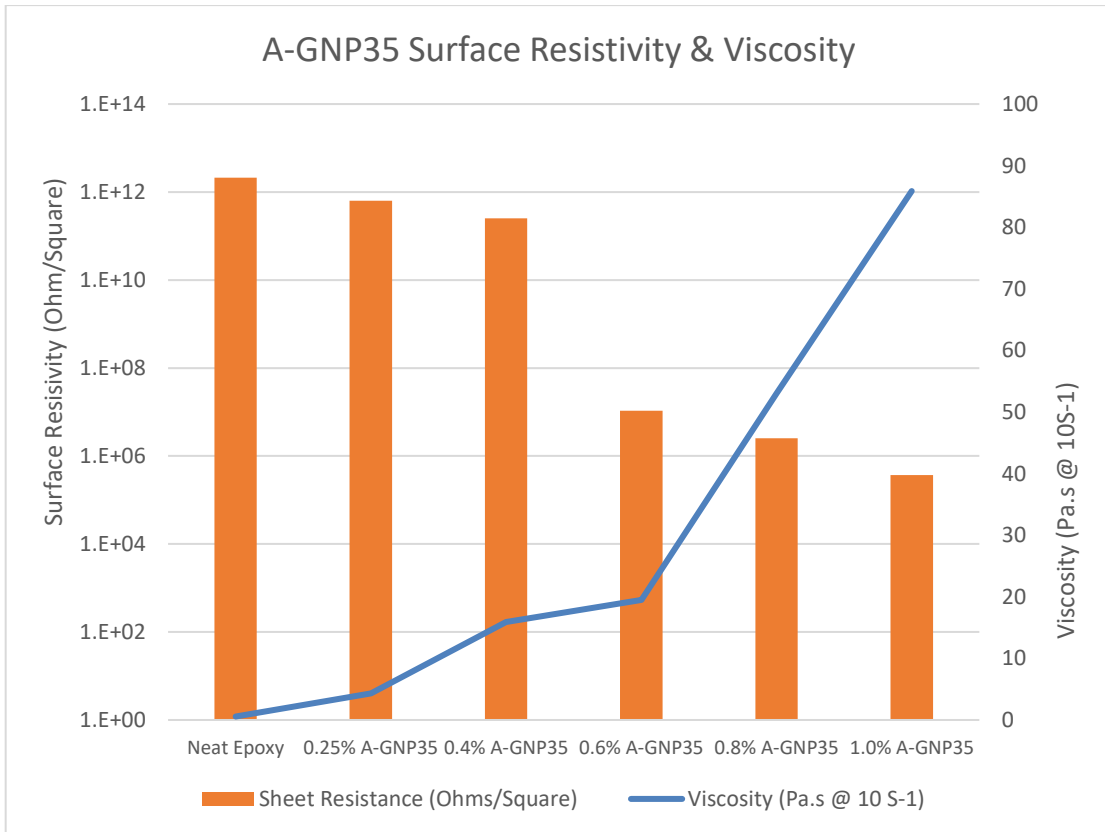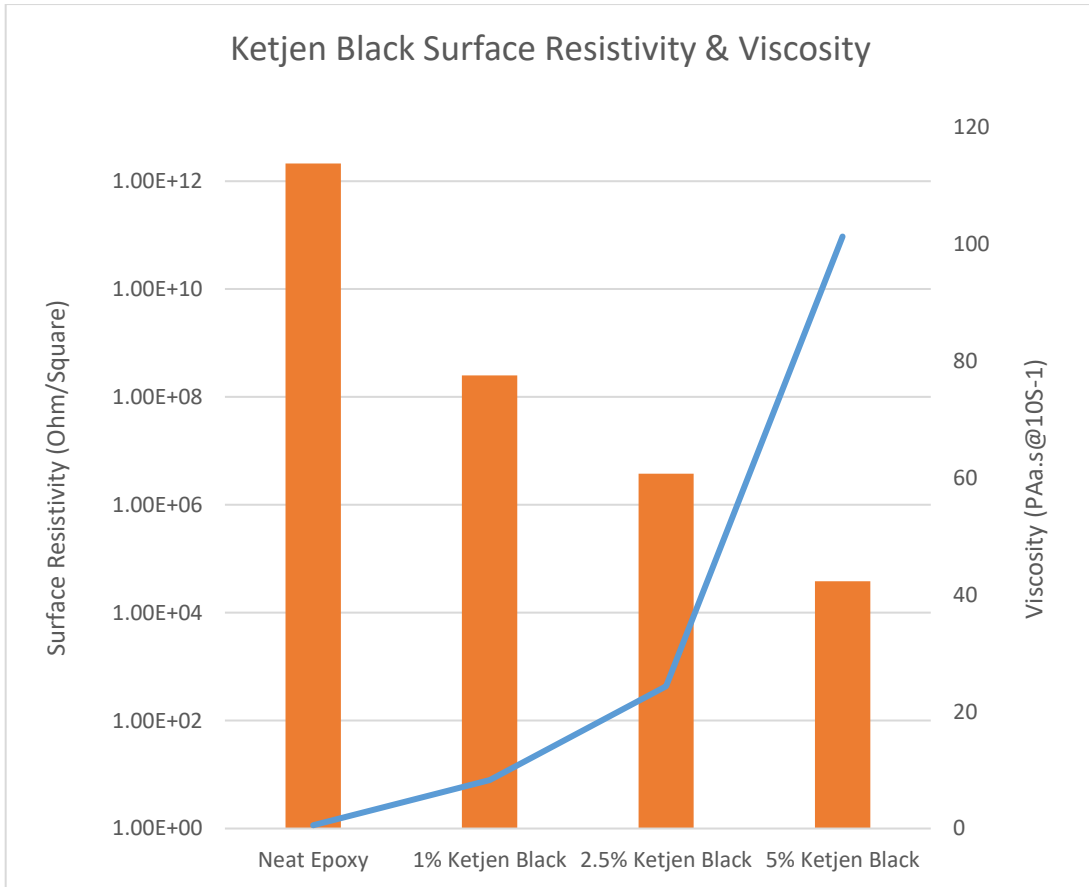
3.3. Discussion

The Ketjen Black had a lower impact on viscosity, making it possible to achieve 5% w/w loading.

However the A-GNP35 graphene demonstrated higher levels of conductivity on equivalent loadings (by weight). At 1% w/w the graphene had a surface resistivity of 3.71×10^5 Ω/square whereas the Ketjen black had a surface resistivity of 2.5×10^8 Ω/square.
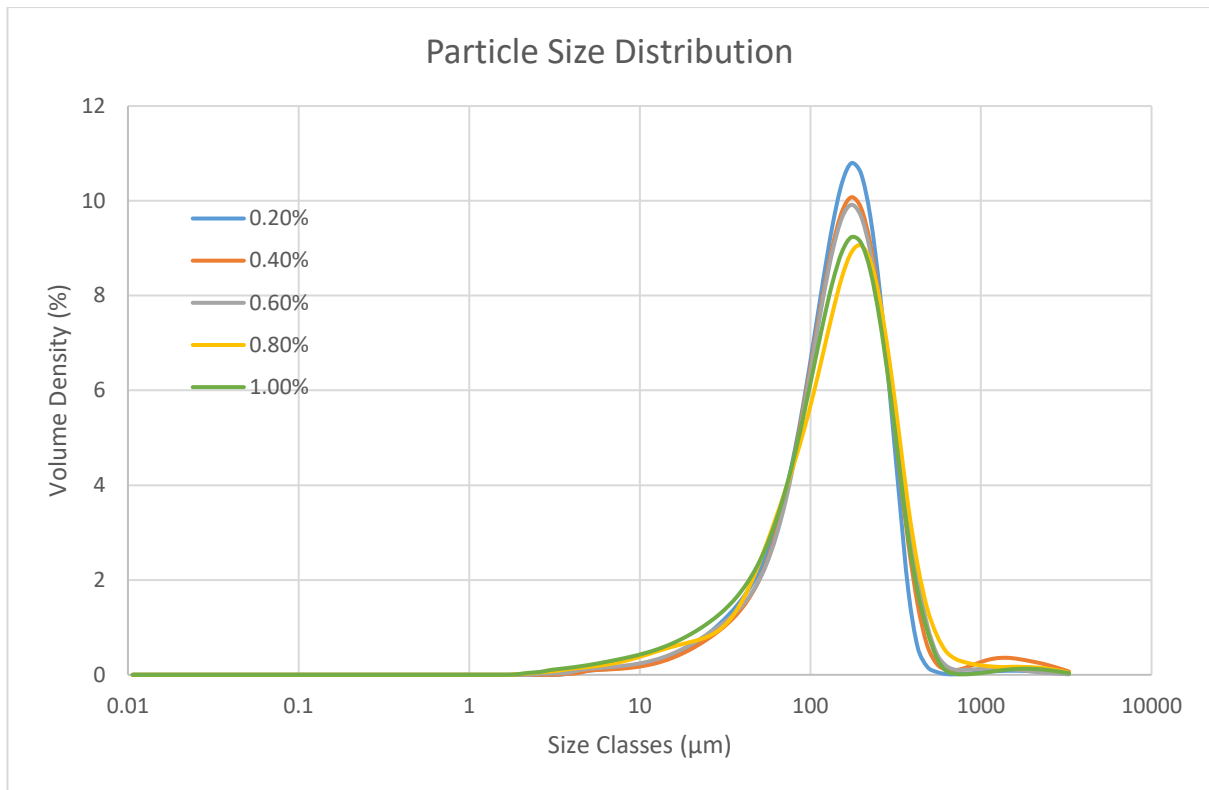
4. Conductivity in Epoxy Resins

4.1. Impact of Loading Level on Electrical Conductivity in an Epoxy Coating

This work was carried out to understand the relationship between graphene loading level and conductivity. The graphene was added to the epoxy (EEW = 190 g/eq) using a Thinky mixer to ensure the graphene nano platelets would remain at their largest size, as it was presumed from earlier work that the larger the particle size the greater the level of electrical conductivity.
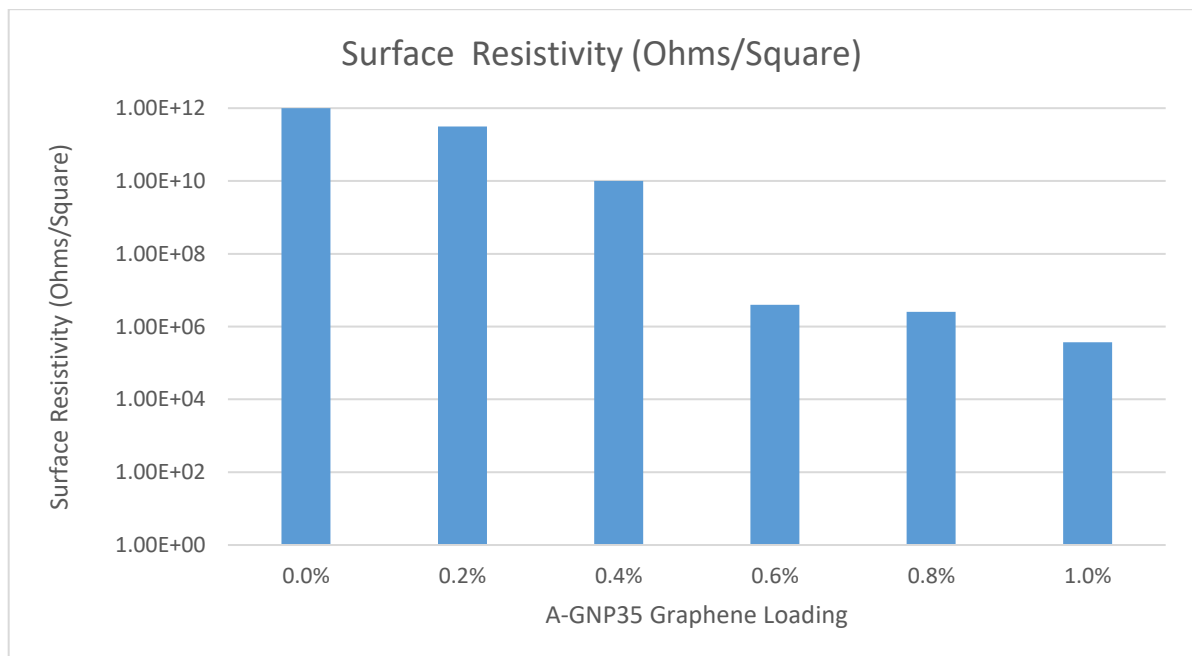
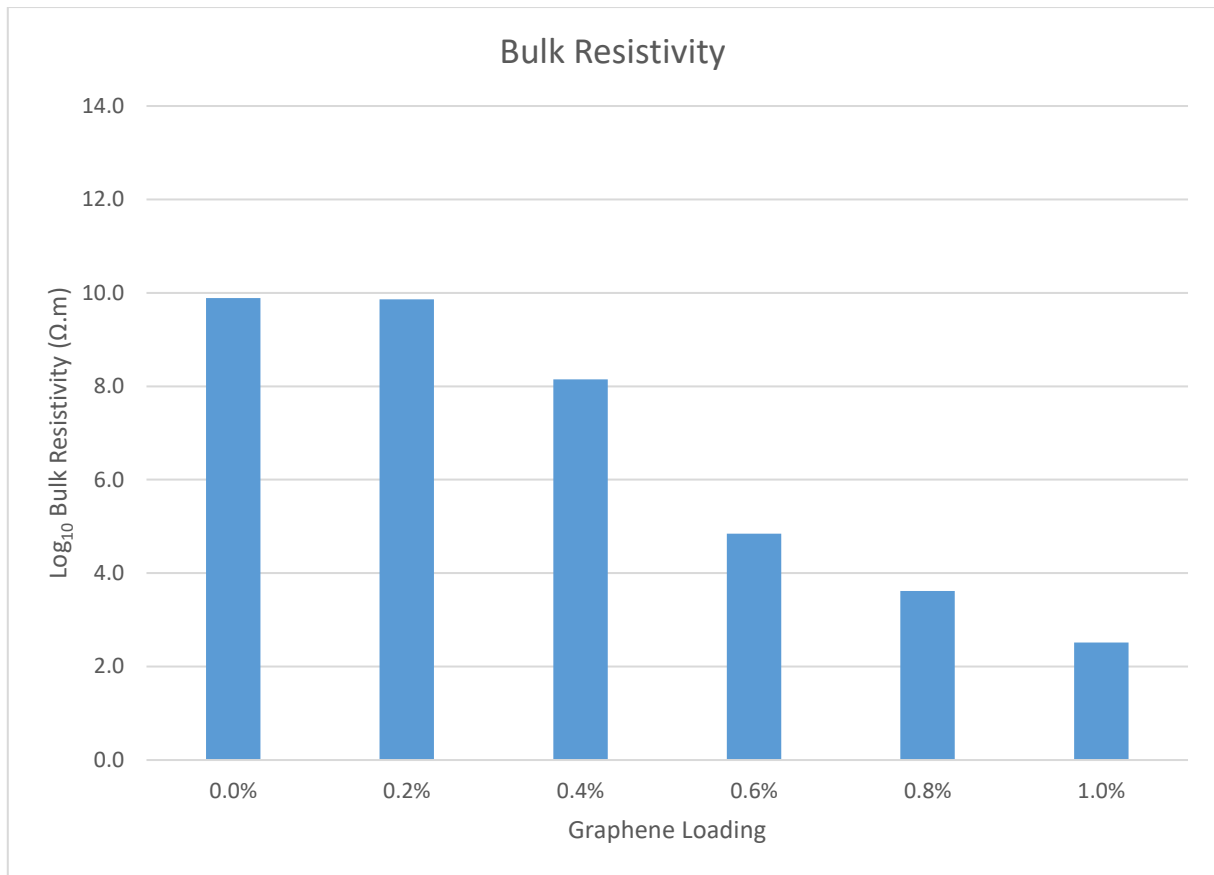The epoxy to Epikure 3234 hardener mix ratio was 100 to 13.

The resulting Particle Size Distribution is given in the table below:

Sample (%wt Graphene)	Dx(10) (µm)	Dx(50) (µm)	Dx(90) (µm)
0.2%	50.7	149	279
0.4%	54.8	155	315
0.6%	50.4	153	314
0.8%	45.4	157	341
1.0%	38.1	146	305

Particle Size Distribution

Volume Density (%) vs Size Classes (μm)

Legend:
- 0.20%
- 0.40%
- 0.60%
- 0.80%
- 1.00%

4.1.1. Electrical Conductivity

Surface Resistivity (Ohms/Square)

Surface Resistivity (Ohms/Square) vs A-GNP35 Graphene Loading

Bulk Resistivity

Conductivity data has shown that an increase in graphene loading reduces both bulk resistivity and surface resistivity. The levelling off that appears at 0.6% loading level suggests that it is the percolation threshold for A-GNP35 in an epoxy matrix.

4.2. Effect of Particle Size on Conductivity in Epoxy Dispersions

Previous work had shown that particle size can have an impact on electrical conductivity. This work was carried out to demonstrate the relationship between particle size and electrical conductivity, as well as to identify a possible optimum particle size distribution for conductive applications.

The graphene was added to two epoxies (i) EEW = 190 g/eq and (ii) EEW=250g/eq) using a Thinky mixer to ensure the graphene nano platelets would initially remain at their largest size. It was presumed from earlier work that the larger the particle size the greater the level of electrical conductivity. The samples were then further milled using a three roll mill to reduce the PSD of the samples.

Processing Summary: This is outlined in the table below describing how the various samples were processed.
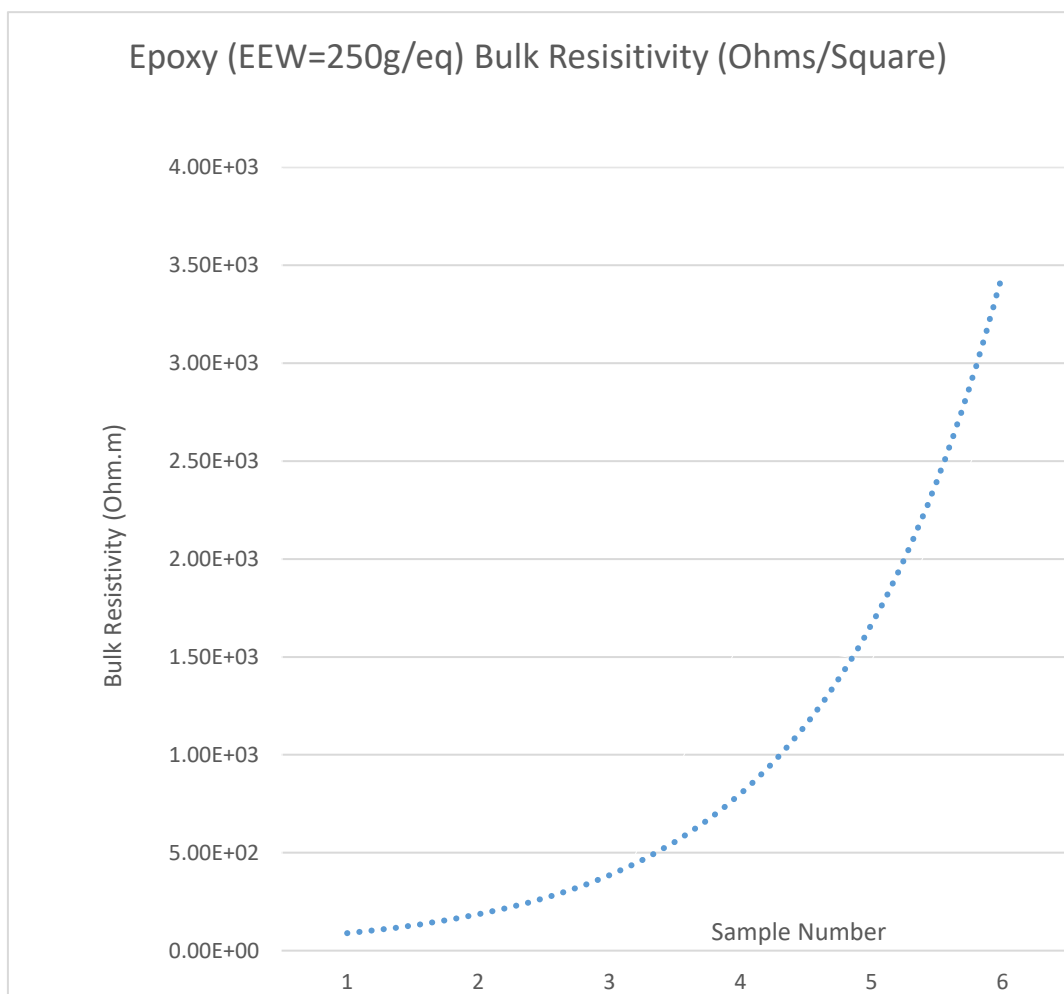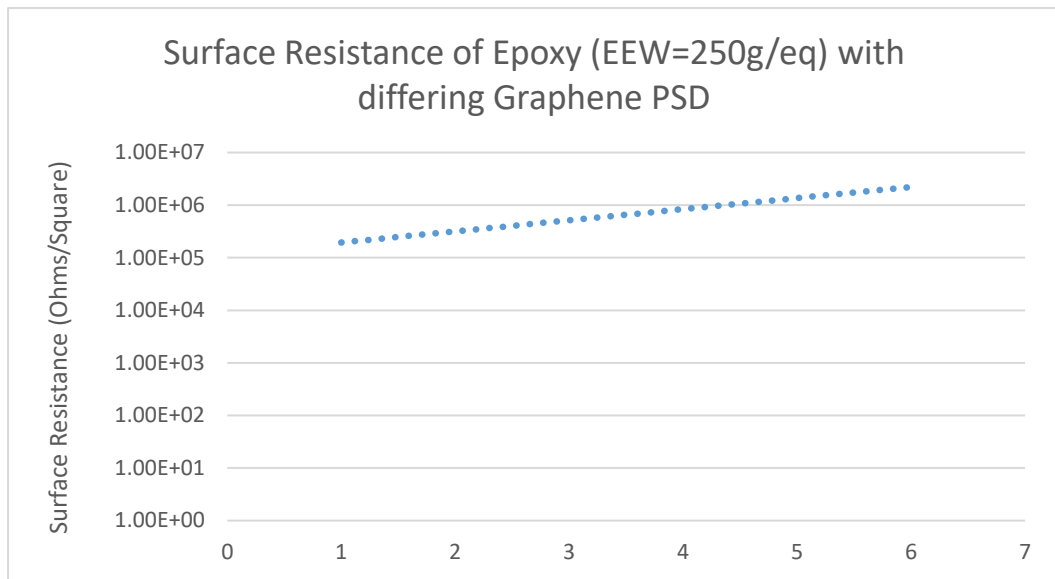
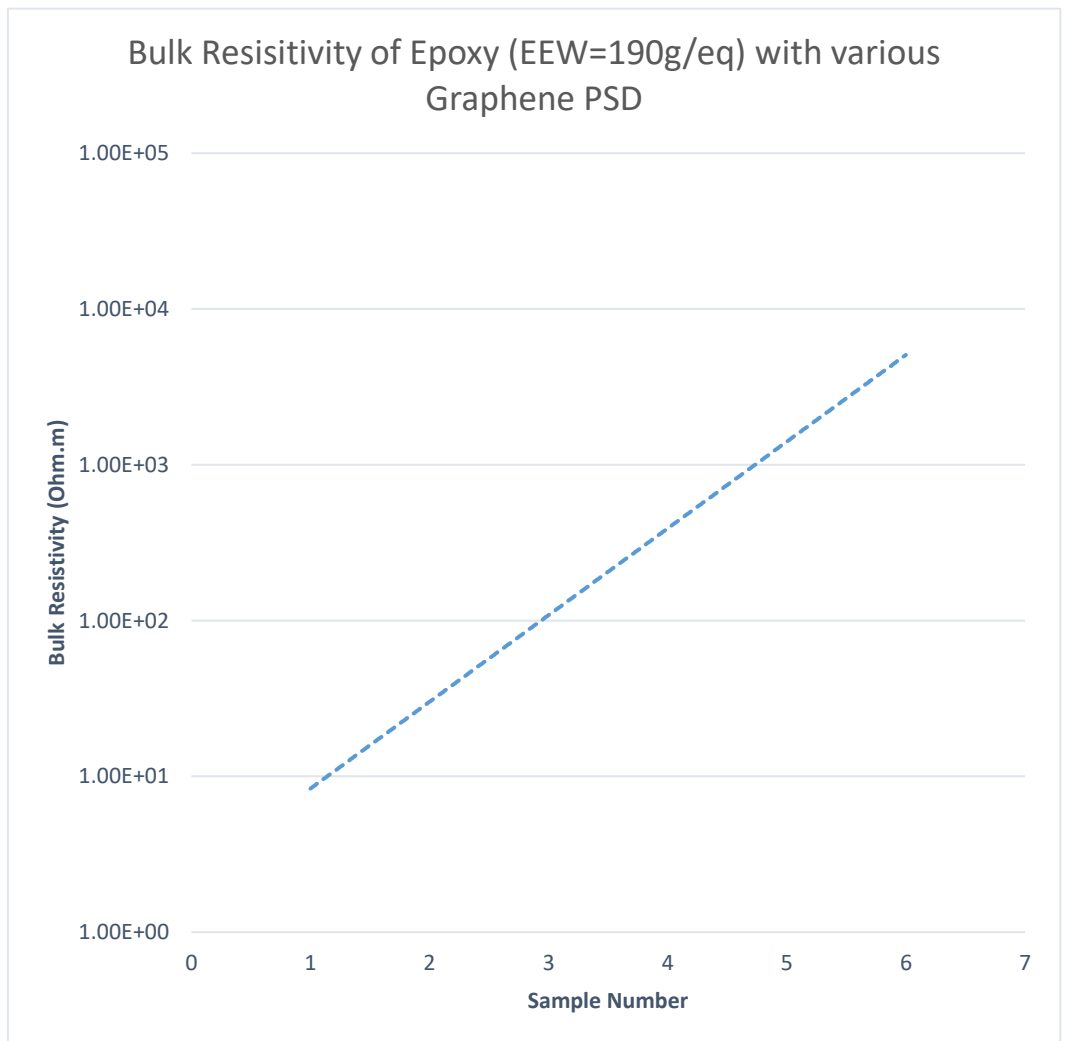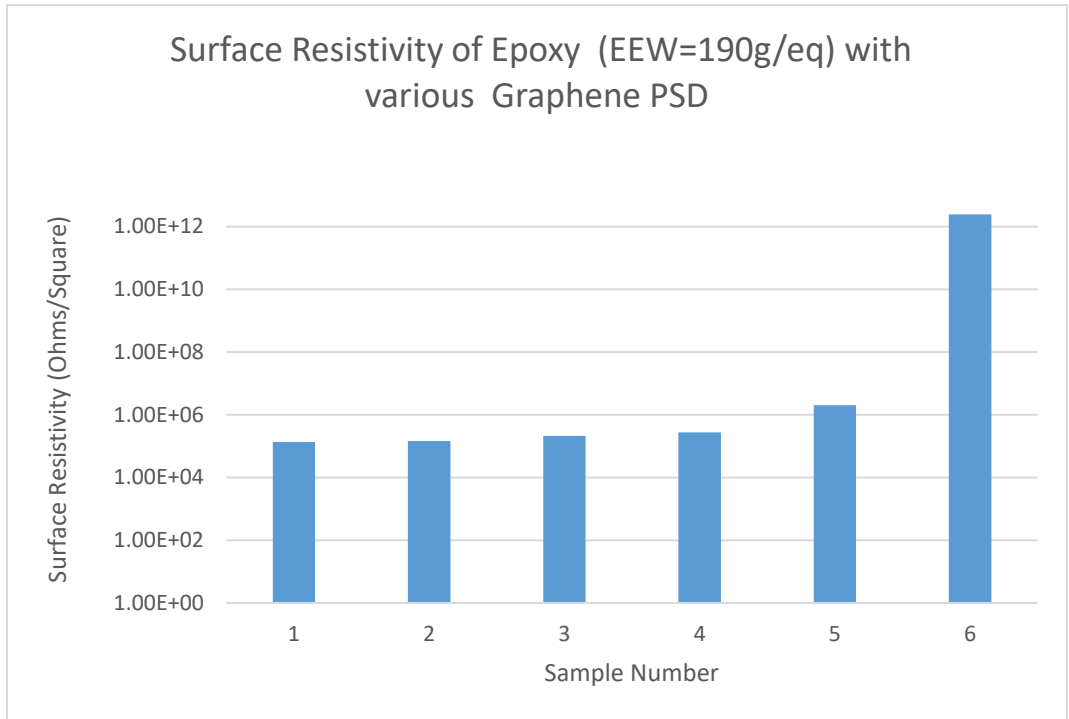| Sample Number	Milling steps
1	Thinky mix only
2	Thinky mix + 1 pass in a Three Roll Mill at 60 μm /20 μm gap size
3	As above + 30 μm /10 μm gap size
4	As above + 15 μm / 5 μm gap size
5	As above + 6 passes at 15 μm /5 μm
6	As above + 6 passes on force mode at 5N/mm

4.2.1. Particle Size Distribution

Epoxy resin (EEW=250 g/eq)	Dx(10) (μm)	Dx(50) (μm)	Dx(90) (μm)
1	4.75	47.7	141
2	0.03	5.74	14.1
3	0.03	4.42	10.6
4	0.37	4.25	12.8
5	0.02	3.25	10.6
6	0.02	1.86	6.44

EEW=190 (g/eq)	Dx(10) (μm	Dx(50) (μm)	Dx(90) (μm)
1	36.2	154	382
2	4.52	43.6	146
3	2.06	34.6	103
4	0.72	25.2	71.6
5	0.02	1.28	25.9
6	0.02	0.886	21.7

4.2.2. Electrical Conductivity

Surface Resistance of Epoxy (EEW=250g/eq) with differing Graphene PSD

Epoxy (EEW=250g/eq) Bulk Resisitivity (Ohms/Square)

Surface Resistivity of Epoxy (EEW=190g/eq) with various Graphene PSD

Bulk Resistivity of Epoxy (EEW=190g/eq) with various Graphene PSD

For both epoxy resins (EEW=190 g/eq and EEW=250 g/eq) as expected, more milling steps yielded a lower particle size distribution.

With the 250 g/eq epoxy the particle size distribution dropped very rapidly before tailing off, whereas for the 190 g/eq epoxy the harsher milling programme only caused a gradual change in the distribution profile indicating that the two epoxies do not mill in quite the same manner when subjected to the same conditions.

In electrical conductivity tests, for both epoxies, more and harsher milling steps gradually increases both the surface resistivity and bulk resistivity. In conclusion the data suggests there is a link between particle size and electrical conductivity; larger particle sizes are generally favourable for electrical conductivity.

5. Conductivity in Solvents

5.1. Effect of Particle Size on Conductivity in Solvent Based Dispersions

Previous work has shown that particle size of A-GNP35 graphene can have an impact on electrical conductivity. The aim of this work is to identify an optimum particle size distribution for conductive applications in the solvent-based dispersions.

Dispersing Resin was added to butyl acetate and roller mixed to produce a stock solution of dispersing resin in butyl acetate. A-GNP35 was added to the dispersing resin solution to give 0.5% by weight of A-GNP35). This dispersion was passed once through and samples taken as the dispersion exited the mill. The remaining dispersion was repeatedly passed through the mill in the same manner, sampling in the same way at pass 3, pass 6, pass 9, pass 12 and pass 15.
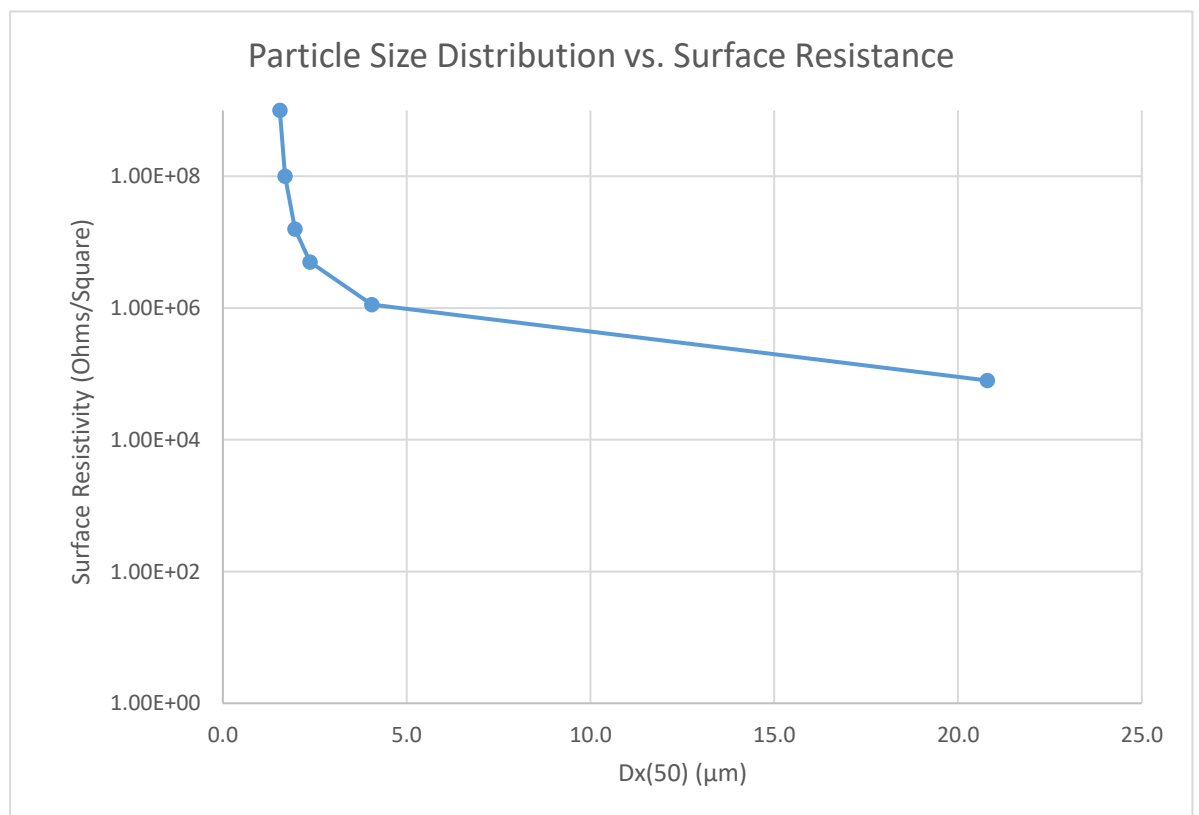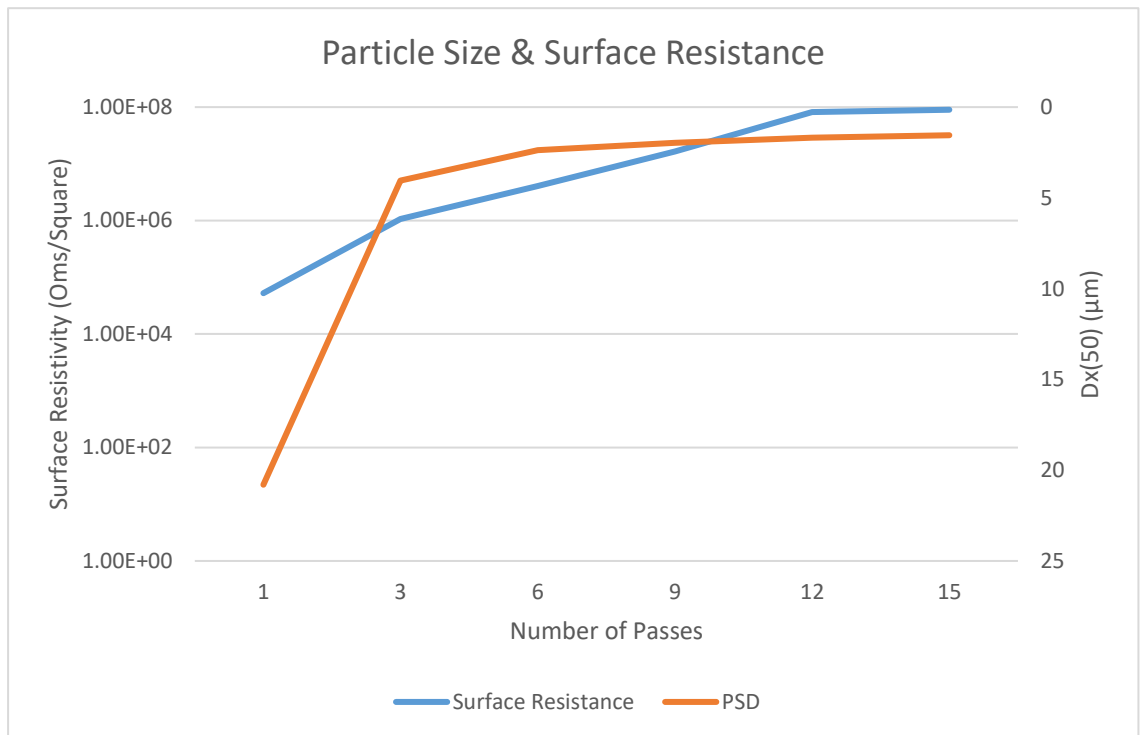
Each sample was drawn down onto two colour cards at 600 µm thickness and left to harden for 2 days at room temperature. Each colour card was measured for surface resistivity.

5.2. Results

5.2.1. Particle Size Distribution

Sample	Dx(10) (µm)	Dx(50) (µm)	Dx(90) (µm)
Pass 1	2.73	20.8	73.7
Pass 3	0.03	4.05	19.4
Pass 6	0.02	2.37	8.28
Pass 9	0.02	1.96	8.48
Pass 12	0.02	1.69	6.15
Pass 15	0.02	1.55	9.19

5.2.2. Electrical Conductivity

Particle Size & Surface Resistance

Particle Size Distribution vs. Surface Resistance

Electrical conductivity testing indicated a clear trend in increasing surface resistance with increasing number of passes.

Dispersion with D90>70µm gave the best conductivity. Conductivity dropped as particle size distribution went up.

6. Conductivity in Pigmented Paints

6.1. Comparing Conductivity of Pigmented Paint Containing Graphene and Ketjen Black

Two conductive dispersions at 1% wt/wt were prepared in an epoxy (EEW=250g/eq). One loaded with A-GNP35 graphene and the other loaded with Ketjen Black. Each of the dispersions were added to a pigmented epoxy paint to achieve 0.25% and 0.5% loading in the final paint.

Part A: Epoxy Base

| Item | Raw material name | Control | Weight % | |
			Control with 0.25% A-GNP35 or 0.25% Ketjen Black	Control with 0.5% A-GNP35 or 0.5% Ketjen Black
Charge items 1,2,3 ,4 and 5 and mix at high speed (2000 rpm) for 10 minutes				
1	Epoxy Resin (EEW= 250g/eq.)	11.34	9.98	9.98
2	Cymel U-216 resin	0.25	0.22	0.22
3	Anti-terra U	0.41	0.36	0.36
4	Xylene	7.84	6.90	6.90
5	Tixogel MP	0.37	0.33	0.33
Check Gel is homogenous and free of bits. Continue mixing if not.				
Add items 6 to 8. Mix at high speed (2000 rpm) for 15 minutes. Check grind <25 microns				
6	Butanol	2.02	1.78	1.78
7	Titanium dioxide	11.18	9.84	9.84
8	Blanc Fixe	44.47	39.15	39.15
Add items 9,10 & 11. Mix at medium speed (1000rpm) for 15 minutes.				
9	0.25% 0r 0.5% of A-GNP35 or Ketjen Black in EEW=250g/eq	0	0.25	0.5
10	Epoxy Resin (EEW=250g/eq.)	14.17	24.75	24.5
11	Xylene	7.84	0	0

Part B: Amine Hardener

Item	Raw Material Name	Weight %	Weight %	Weight %
12	Amine Hardener	4.27	5.77	5.77

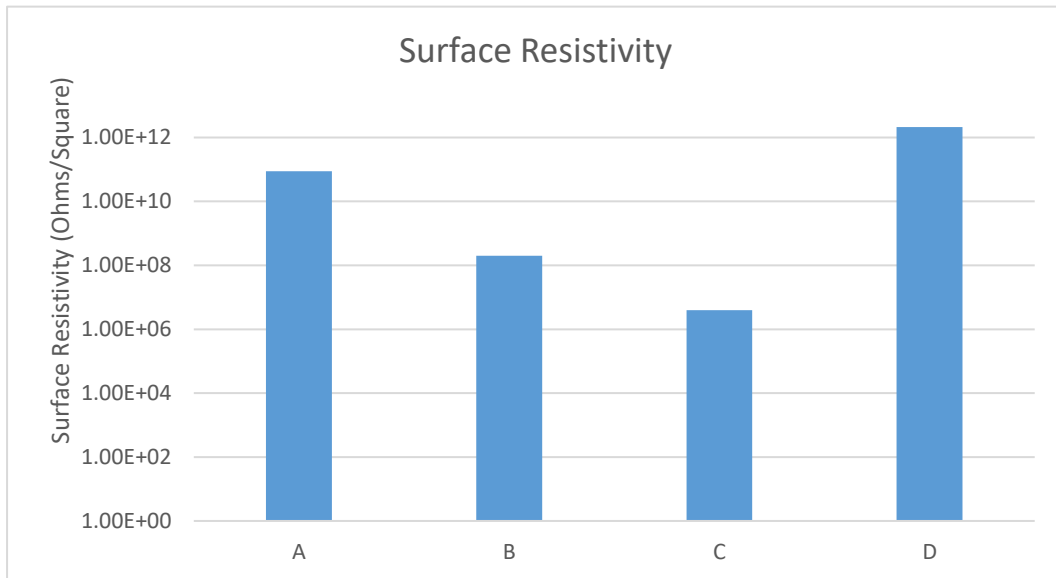|				
pvc	35	37	37
VOC (g/l)	320	156	156

Surface Resistivity
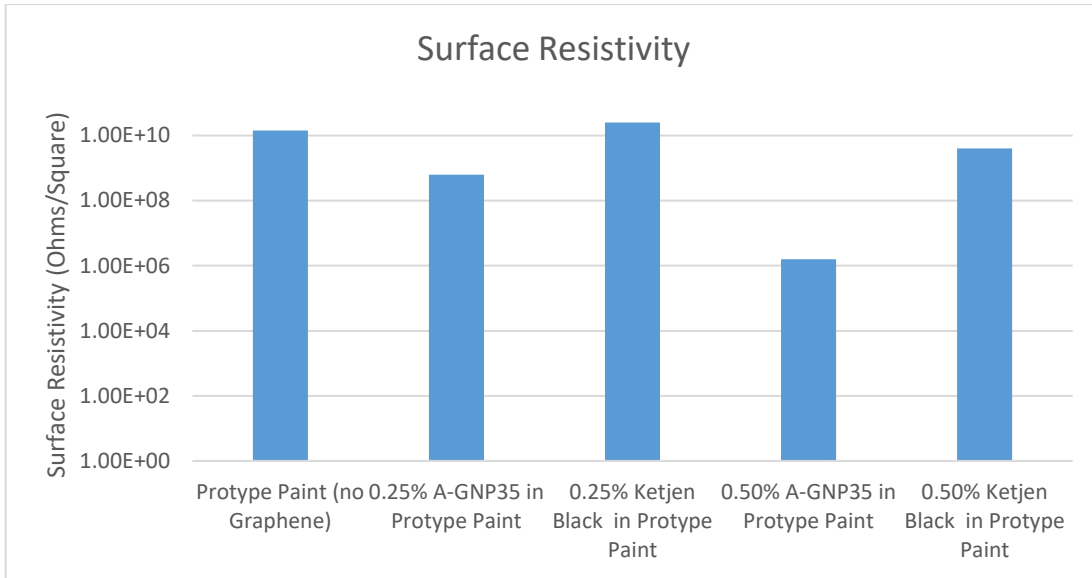
1% A-GNP35 was added to epoxy resin that had been diluted to give a range of solids contents.

Lower solids content (60% w/w) gave the lowest resistivity levels.

Surface Resistivity vs. Solid Contents
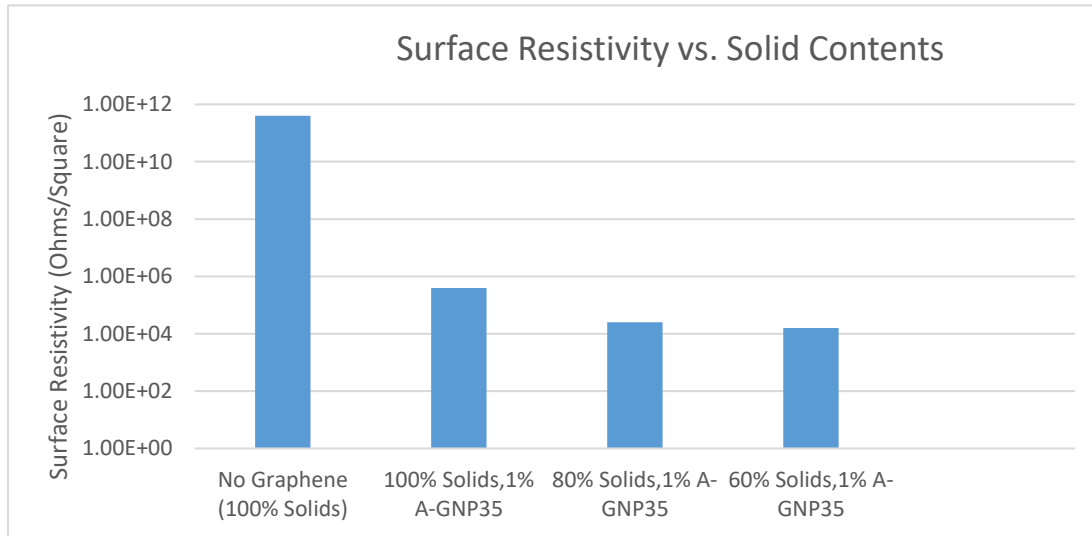
Lower solids content (60% w/w) gave the lowest resistivity levels.

6.2. Surface Resistivity of Graphene dispersed in Commercially Available Epoxy Primers

A-GNP35 graphene was dispersed at 1% wt in the amine hardener component of two commercially available epoxy primers. These were cured with the corresponding pigmented epoxy base and the measured surface resistance levels are shown in the charts below.

Surface Resistivity

Chart: Surface Resistivity (Ohms/Square) vs samples A, B, C, D. Y-axis logarithmic from 1.00E+00 to 1.00E+12.

		A-GNP35 loading in final paint
A	Commercial Primer A (with 1% Graphene in Hardener)	0.20%
B	Commercial Primer B (with 1% Graphene in Hardener)	0.25%
C	Prototype Primer with amine hardener (with 1% Graphene in Hardener)	0.17%
D	Prototype Primer with no addition of Graphene in Hardener)	0.00%

Bulk and surface resistivity results suggest the final GNP loading is dependent on mix ratio and is driving the variation in level of conductivity. The addition of 1% wt graphene in the hardener of the prototype primer resulting in an overall loading of graphene at 0.17% wt demonstrates that static dissipative levels of conductivity can be readily achieved as defined in the ESD materials categories shown in section 2.

7. Summary

GNP particle size has an impact on final conductivity with larger platelets producing dispersions with higher levels of conductivity. The greater the level of milling, the lower the PSD which increases both the bulk and surface resistivity levels.

Graphene loading level plays a key role in resistivity levels. The higher the loading, the lower the resistivity level.

As expected, the lateral dimensions of the graphene nanoplatelets can have an impact on percolation thresholds, highlighting the importance of using the correct milling and incorporation techniques for initial dispersion and addition to the coating formulation.

Lower resistivity levels can be achieved by reducing the mass solids of the dispersion (i.e. increasing the ratio of graphene to resin)

Graphene can be dispersed into epoxies to readily achieve surface resistivity's that would impart the epoxy with static dissipative capabilities and in some cases would give a level of surface resistance that would lie in the range of the conductive composites category for ESD material *(ref: www.pac.on/art-esd-resistivity)*

Graphene could be dispersed into the amine hardener component of an epoxy paint rather than into the epoxy paint. However, mix ratios would have to be modified to achieve higher loadings in the final paint film.