ELECTRICAL PROPERTIES OF GRAPHENE/VINYL ESTER COMPOSITES

Lashkari, P[1], Martin, E[2], Divigalpitiya, R[3] and Hrymak, A[1*]

1. Department of Chemical and Biochemical Engineering, University of Western Ontario, London, Ontario, Canada
2. Fraunhofer Innovation Platform for Composites Research, University of Western Ontario, London, Ontario, Canada
3. HydroGraph Clean Power Inc., London, Ontario, Canada N6G 4X8

* Corresponding author (ahrymak@uwo.ca)

Keywords: *Polymer Composites, Graphene, Bipolar Plates*

ABSTRACT

Fractal Graphene (FG) is an ultra-high purity turbostratic form of graphene which is synthesized by a controlled detonation of acetylene and oxygen. This process is novel, one-step, highly efficient, gas-phase and environmentally friendly, which yields pristine graphene nanosheets. This research focuses on fabrication of highly filled FG based vinyl ester composites and investigates the electrical properties of the obtained composites. Polymer composites are developed by compression molding of vinyl ester as a binder and conductive fillers Graphite 3243, Graphite A99 and Ketjenblack EC-600JD (CB) and Fractal Graphene (FG) as secondary fillers. The study investigates various formulations of graphite, CB and FG. The FG component varied from 0 wt.%, to 0.09 wt.% while maintaining 50 wt.% total carbon filler. Low FG addition significantly enhances both through plane and in-plane conductivity compared to other formulations of the named carbon fillers. Additionally, Carbon Black (CB) shows the most significant statistical effects in the experimental study.

1 INTRODUCTION

Graphene-polymer composites are advanced materials that combine the unique properties of graphene with the flexibility and processability of polymers[1], [2], [3]. Vinyl ester resin (VE) is a thermosetting resin known for its outstanding overall performance, and it has demonstrated extensive potential applications in sectors such as defense, aerospace, transportation, and various other fields[4]. A Design of Experiments (DoE) was conducted to understand the effects of various carbon fillers on electrical conductivity of vinyl ester/graphene composites. In previous literature, it has been demonstrated that combinations of different types of graphite enhances the polymer composite electrical conductivity[5], [6]. The response output are through-plane conductivity (TPEC) and in-plane conductivity (IPEC).

2 MATERIALS AND PREPARTAION OF COMPOSITES

Vinyl ester Derakane 782 used in this study was supplied by INEOS. The organic peroxide used was Trigonox C (tert-butylperoxybenzoate), supplied by Nouryon. Fractal graphene (FG) was supplied by Hydrograph Clean Power Inc. (Vancouver, Canada). Graphite was used as the primary filler, prepared by combination of synthetic graphite (Asbury carbons A99) and natural graphite flake (Asbury Carbon GP3243). The particle size of synthetic graphite and flake graphite was 20 and 45 µm, respectively, table 1 shows the particle size distribution for both the graphite. The carbon black (CB) used in this study was Ketjenblack EC-600JD which has a high surface area of 1400 m^2 /g. Release film Wrightlon 5200 (Airtech Advanced Materials Group) was used a mold release for this study.

Table 1 Particle size distribution of Graphite

Particle Size	A99 (%)	3243 (%)
+100 Mesh (150 Micron)	0	0.2
+200 Mesh (75 Micron)	0.04	12
+325 Mesh (44 Micron)	0.36	26.4
-325 Mesh (44 Micron)	99.61	61.4

The composites were prepared by blending vinyl ester resin, carbon black, graphene, graphite, and initiator with a paddle mixer at a low speed. The blended mixtures were then pressed at 50 bars for 3 min with a Model 2518 Carver Lab Press, which had a mold surface temperature of 150 °C. In total 5 samples were molded for each formulation and molded samples were 100 mm by 100 mm by 3 mm in dimension.

3 CHARACTERIZATION OF COMPOSITES

3.1 Through-Plane Electrical Conductivity

The through-plane electrical conductivity (TPEC) of polymer composite was measured using a purpose built two probe test apparatus. Sample surfaces were cleaned to remove dust with a paper towel. The electrical resistance (R, Ω) of the circuit was determined along the using a Keithley 2700 multi meter (Tektronix Inc., Beaverton, Oregon). The electrical conductivity (σ) for each sample was calculated by taking the sample dimensions into consideration. To improve the contact between surfaces of the specimen and the copper electrode pressure was applied using a hydraulic press. The electrical conductivity (σ) of the samples can be expressed using equations 1 and 2 shown below. In the equations, ρ is resistivity, A the cross-sectional area of the sample, L the thickness of the same, Ro, Rs and R, are total resistance, circuit resistance and sample resistance, respectively.

$$\rho = \mathrm{R}\frac{\mathrm{A}}{\mathrm{L}} = \frac{(\mathrm{Ro}-\mathrm{Rs})A}{L} \qquad (1)$$

$$\sigma = \frac{1}{\rho} \qquad (2)$$

3.2 Ossila In-Plane Electrical Conductivity

The surface in-plane electrical conductivity (IPEC) was measured using an Ossila T2001A3 4-point probe instrument. The electric current was passed between the outer two probes and the change in the voltage was recorded across the inner two probes [7]. The electrical conductivity was measured at center and corners for each part and mean values were reported for the parts using a 4-point probe.

3.3 Bulk-In-Plane Electrical Conductivity

The bulk in-plane electrical conductivity was measured using a two-point probe setup similar to the through-plane electrical conductivity. Firstly, a 20 mm *10 mm test specimen was cut from 100 mm * 100mm panel and sample surfaces were cleaned to remove dust with a paper towel. The electrical resistance was measured using a Keithley 2700 multimeter (Tektronix Inc., Beaverton, Oregon) and calculations were done to get conductivity according to the equation mentioned in section 3.1.

4 RESULTS AND DISCUSSION

The total filler content for each formulation was constant at 50 wt.% where graphite 3243 was used as primary filler followed by different levels of graphite A99, CB and FG. Natural graphite and synthetic graphite were mixed because according to literature the presence of synthetic micro graphite particles increases the packing factor by filling the gap between the graphite particles [5]. The maximum loading of CB used in this study was 5 wt.%, the same loading has been used by other research groups [8], [9], [10]. The design is based on 27 experimental runs with two output responses. ANOVA was used to study the significance of each input parameter. Table 2 represents the values of the various levels of input and the output response for the DoE.

Table 2 Electrical Conductivity Measurements

Formulation No.	Graphite 3243 (wt. %)	Graphite A99 (wt. %)	Carbon Black (wt. %)	Graphene (wt. %)	Output Responses (S/cm)		
					Ossila In-Plane	Through Plane	Bulk In-Plane
1	50.0	0.0	0.0	0.0	2.40 ± 0.1	0.26 ± 0.1	0.82 ± 0.0
2	42.5	7.5	0.0	0.0	1.48 ± 0.2	0.19 ± 0.0	0.53 ± 0.0
3	35.0	15.0	0.0	0.0	1.67 ± 0.1	0.24 ± 0.1	0.47 ± 0.0
4	48.0	0.0	2.5	0.0	7.68 ± 0.7	1.09 ± 0.2	2.56 ± 0.1
5	40.0	7.5	2.5	0.0	6.64 ± 0.9	1.08 ± 0.1	2.53 ± 0.1
6	33.0	15.0	2.5	0.0	6.03 ± 0.5	0.48 ± 0.0	1.96 ± 0.0
7	45.0	0.0	5.0	0.0	8.60 ± 0.5	1.36 ± 0.3	2.86 ± 0.2
8	37.5	7.5	5.0	0.0	6.22 ± 0.7	1.00 ± 0.1	2.30 ± 0.1
9	30.0	15.0	5.0	0.0	4.83 ± 0.5	1.37 ± 0.2	1.75 ± 0.1
10	48.0	0.0	0.0	2.0	4.91 ± 0.7	0.23 ± 0.0	1.23 ± 0.1
11	41.0	7.5	0.0	2.0	5.20 ± 0.3	0.54 ± 0.0	1.96 ± 0.1
12	33.0	15.0	0.0	2.0	4.05 ± 0.4	0.43 ± 0.0	1.35 ± 0.0
13	45.5	0.0	2.5	2.0	8.05 ± 1.9	1.66 ± 0.3	2.28 ± 0.1
14	38.0	7.5	2.5	2.0	4.07 ± 0.3	0.50 ± 0.0	1.32 ± 0.1
15	30.5	15.0	2.5	2.0	3.97 ± 0.8	0.55 ± 0.0	1.41 ± 0.1
16	43.0	0.0	5.0	2.0	6.54 ± 1.0	1.60 ± 0.7	2.12 ± 0.4
17	36.0	7.5	5.0	2.0	2.27 ± 0.2	1.13 ± 0.3	0.94 ± 0.1
18	28.0	15.0	5.0	2.0	4.98 ± 0.7	0.58 ± 0.0	1.76 ± 0.1
19	46.0	0.0	0.0	4.0	5.43 ± 0.5	0.30 ± 0.0	1.81 ± 0.0
20	38.5	7.5	0.0	4.0	5.76 ± 0.4	0.30 ± 0.0	1.92 ± 0.1
21	31.0	15.0	0.0	4.0	4.91 ± 0.5	0.42 ± 0.0	1.49 ± 0.0
22	44.0	0.0	2.5	4.0	5.87 ± 0.4	1.45 ± 0.3	1.71 ± 0.1
23	36.0	7.5	2.5	4.0	7.93 ± 0.5	1.66 ± 0.7	2.51 ± 0.3
24	29.0	15.0	2.5	4.0	7.41 ± 0.4	1.47 ± 0.6	2.97 ± 0.2
25	41.0	0.0	5.0	4.0	3.88 ± 0.3	0.49 ± 0.0	1.49 ± 0.0
26	33.5	7.5	5.0	4.0	3.11 ± 0.6	0.61 ± 0.0	1.64 ± 0.0
27	26.0	15.0	5.0	4.0	3.42 ± 1.0	1.96 ± 0.8	1.95 ± 0.3

4.1 Effects of Graphite A99, Carbon Black and Fractal Graphene On In-Plane Electrical Conductivity

Figure 1 shows the main effects of the different fillers on the electrical conductivity. The plot suggests that the in-plane electrical conductivity measured by the Ossila apparatus is influenced differently by each of the three factors. CB at a 2.5 wt.% greatly increases conductivity, but higher levels may be deleterious. The A99 graphite shows less pronounced effect and FG seems to decrease conductivity as its level increases.

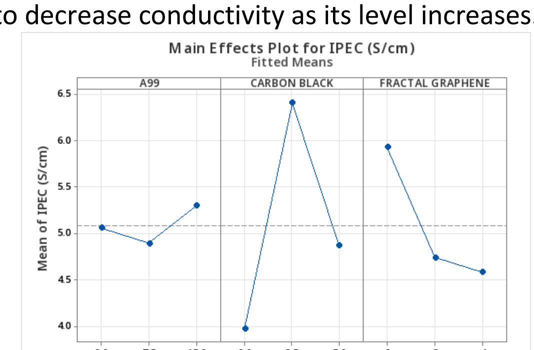

Figure 1 Main effect plots for IPEC (S/cm)

From an Analysis of Variance as shown in Table 3, it can be concluded that the Carbon Black and its interaction with A99 are significant factors affecting the in-plane electrical conductivity of the composites. FG single factor is slightly above the p=0.05 test threshold, but its two-factor interactions with the other factors are not significant. The A99 Graphite does not appear to have a significant effect on its own.

Table 3 Analysis of Variance for IPEC

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	18	91.187	5.0659	4.26	0.021
Linear	6	37.586	6.2643	5.27	0.018
A99	2	0.760	0.3802	0.32	0.735
CARBON BLACK	2	27.114	13.5568	11.40	0.005
FRACTAL GRAPHENE	2	9.712	4.8559	4.08	0.060
2-Way Interactions	12	53.601	4.4668	3.76	0.034
A99*CARBON BLACK	4	39.844	9.9610	8.38	0.006
A99*FRACTAL GRAPHENE	4	9.370	2.3426	1.97	0.192
CARBON BLACK*FRACTAL GRAPHENE	4	4.387	1.0967	0.92	0.496
Error	8	9.512	1.1890		
Total	26	100.699			

4.2 Effects of Graphite A99, Carbon Black and Fractal Graphene on Through-Plane Electrical Conductivity

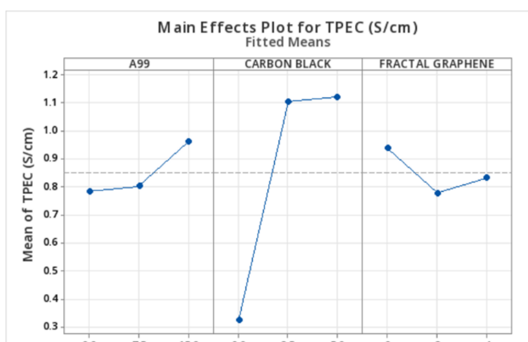

Figure 2 Main effect plots for TPEC (S/cm)

The 2-way interactions between factors do not appear to be significant, as all their p-values are well above 0.05. In summary, based on this ANOVA table, CB is the only factor that significantly affects the through plane electrical conductivity while two-way interactions are not statistically significant effect. Figure 3 shows the main effects of different fillers on the through plane electrical conductivity.

Table 4 Analysis of Variance for TPEC

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	18	6.4841	0.36023	2.18	0.131
Linear	6	4.0346	0.67244	4.07	0.036
A99	2	0.1713	0.08563	0.52	0.614
CARBON BLACK	2	3.7460	1.87301	11.34	0.005

FRACTAL GRAPHENE	2	0.1174	0.05868	0.36	0.711
2-Way Interactions	12	2.4494	0.20412	1.24	0.392
A99*CARBON BLACK	4	0.7526	0.18814	1.14	0.404
A99*FRACTAL GRAPHENE	4	1.0814	0.27036	1.64	0.256
CARBON BLACK*FRACTAL GRAPHENE	4	0.6154	0.15386	0.93	0.492
Error	8	1.3211	0.16514		
Total	26	7.8052			

4.3 Effects of Low Graphene Loadings (< 0.1%wt) on Electrical Conductivity

In the preceding analysis, it was illustrated that high amount of FG loading of 2 wt.% and 4 wt.% have negative impact on the electrical conductivity. Therefore, there was the need to investigate impacts of fractal graphene at low concentration. As a result,, the study was conducted with FG loading below 0.1% which yielded significantly improved electrical conductivity. The formulations are represented in table 5. For this study natural flake graphite 3243 was used as a primary filler and Fractal graphene was mixed at 0 wt.%, 0.01 wt.%, 0.05 wt.%, and 0.09 wt.% while maintaining 50 wt.% total carbon filler. The through-plane and in-plane electrical conductivity is measured according to the procedures presented above. The results suggested that σ gradually increased with increasing loading fraction of graphene. The addition of 0.09wt.% of graphene increased the through-plane electrical conductivity from 0.08 S/cm to 0.18 S/cm which almost two times as compared to formulation with no graphene and similar trend is observed for (Ossila) In-plane electrical conductivity.

Table 5 Graphene experiment batch formulation information.

Formulation #	Graphite 3243 wt.%	Fractal Graphene wt.%
1	50	0
2	49.99	0.01
3	49.95	0.05
4	49.91	0.09

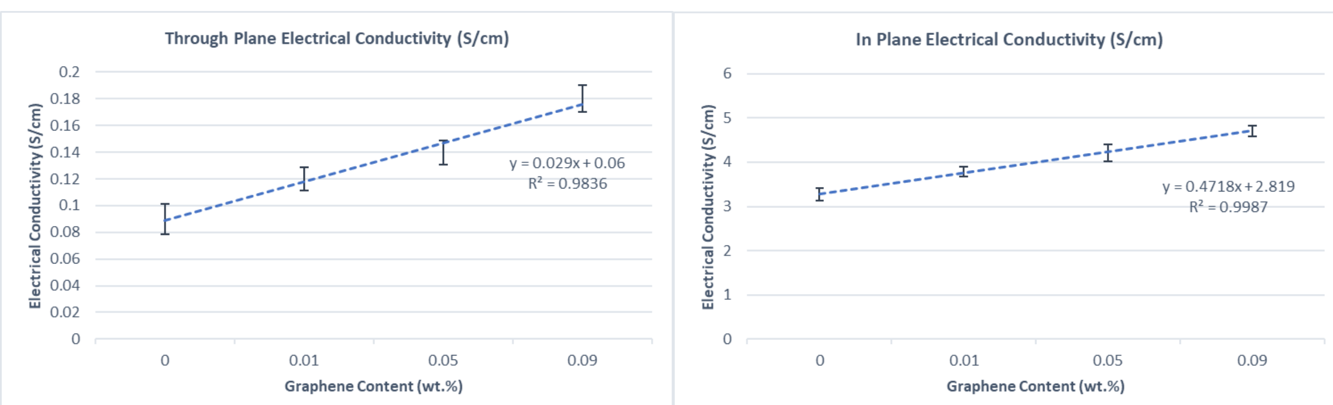

Figure 3 Through-plane (S/cm) and In-plane (S/cm) electrical conductivity with graphene content varying up to 0.1 wt.%

5 CONCLUSIONS

In this experimental investigation electrically conductive vinyl ester composites were produced using a paddle mixer followed by compression molding using 4 different conductive fillers i.e., two types of graphite, FG, and CB. The synergistic effects of filler contents at three levels of variation were studied. The formulation with 2.5 wt.% CB and graphite 3243 demonstrated higher values of the response for both through and in-plane electrical conductivity. The addition of CB above 2.5 wt. % was observed to reduce electrical conductivity, CB was the significant factor that affects all types of electrical conductivity while its two-way interactions are not statistically significant . FG single factor is slightly above the p=0.05 test threshold, but its two-factor interactions with the other carbon fillers are not significant. The A99 Graphite does not show any significant effect on its own also its 2-way interactions with other factors are not statistically significant. But when FG was investigated at concentration of FG < 0.1 wt.% shows a significant increment in electrical conductivity.

6 REFERENCES

[1] H. Kim, A. A. Abdala, and C. W. MacOsko, “Graphene/polymer nanocomposites,” *Macromolecules*, vol. 43, no. 16, pp. 6515–6530, Aug. 2010.

[2] J. Wu, W. Pisula, and K. Müllen, “Graphenes as potential material for electronics,” *Chem Rev*, vol. 107, no. 3, pp. 718–747, Mar. 2007.

[3] J. R. Potts, D. R. Dreyer, C. W. Bielawski, and R. S. Ruoff, “Graphene-based polymer nanocomposites,” *Polymer (Guildf)*, vol. 52, no. 1, pp. 5–25, Jan. 2011.

[4] F. A. Cassis and R. C. Talbot, “Polyester and Vinyl Ester Resins,” *Handbook of Composites*, pp. 34–47, 1998,

[5] M. Tariq, | Utkarsh, | Nabeel, A. Syed, | Amir, and H. Behravesh, “Synergistic enrichment of electrically conductive polypropylene-graphite composites for fuel cell bipolar plates,” 2022.

[6] A. Bairan, M. Z. Selamat, S. N. Sahadan, S. D. Malingam, and N. Mohamad, “Effect of Carbon Nanotubes Loading in Multifiller Polymer Composite as Bipolar Plate for PEM Fuel Cell,” *Procedia Chem*, vol. 19, pp. 91–97, Jan. 2016.

[7] S. Witpathomwong, M. Okhawilai, C. Jubsilp, P. Karagiannidis, and S. Rimdusit, “Highly filled graphite/graphene/carbon nanotube in polybenzoxazine composites for bipolar plate in PEMFC,” *Int J Hydrogen Energy*, vol. 45, no. 55, pp. 30898–30910, Nov. 2020.

[8] B. K. Kakati, A. Ghosh, and A. Verma, “Graphene Reinforced Composite Bipolar Plate for Polymer Electrolyte Membrane Fuel Cell,” *ASME 2011 9th International Conference on Fuel Cell Science, Engineering and Technology. Collocated with ASME 2011 5th International Conference on Energy Sustainability, FUELCELL 2011*, pp. 301–307, Mar. 2012.

[9] B. K. Kakati, D. Sathiyamoorthy, and A. Verma, “Electrochemical and mechanical behavior of carbon composite bipolar plate for fuel cell,” *Int J Hydrogen Energy*, vol. 35, no. 9, pp. 4185–4194, May 2010.

[10] K. A. Imran and K. N. Shivakumar, “Graphene-modified carbon/epoxy nanocomposites: Electrical, thermal and mechanical properties,” *J Compos Mater*, vol. 53, no. 1, pp. 93–106, Jan. 2019.