

Electrical Conductivity of Carbon-Filled Polypropylene-Based Resins

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ABSTRACT: Adding conductive carbon fillers to insulating thermoplastic resins increases composite electrical conductivity. Often, as much of a single type of carbon filler is added to achieve the desired conductivity and still allow the material to be molded into a bipolar plate for a fuel cell. In this study, various amounts of three different carbons (carbon black, synthetic graphite particles, and carbon nanotubes) were added to polypropylene resin. The resulting single-filler composites were tested for electrical resistivity (1/electrical conductivity). The effects of single fillers and combinations of the different carbon fillers were studied via a factorial design. The percolation threshold was 1.4 vol % for the composites containing

only carbon black, 2.1 vol % for those containing only carbon nanotubes, and 13 vol % for those containing only synthetic graphite particles. The factorial results indicate that the composites containing only single fillers (synthetic graphite followed closely by carbon nanotubes and then carbon black) caused a statistically significant decrease in composite electrical resistivity. All of the composites containing combinations of different fillers had a statistically significant effect that increased the electrical resistivity. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 425–433, 2009

Key words: composites; fillers; injection molding; nanocomposites

INTRODUCTION

Most polymer resins are electrically insulating. Increasing the electrical conductivity of these resins allows them to be used in other applications. One emerging market for electrically conductive resins is that for bipolar plates for use in fuel cells. The bipolar plate separates one cell from the next, with this plate carrying hydrogen gas on one side and air (oxygen) on the other side. Bipolar plates require high thermal and electrical conductivities (to conduct heat and to minimize ohmic losses).

One approach to improving the electrical conductivity of a polymer is through the addition of a conductive filler material, such as carbon and metal.^{1–14} Often, a single type of graphite powder is used in thermosetting resins (often a vinyl ester) to produce a thermally and electrically conductive bipolar plate material.^{15–18} Thermosetting resins cannot be remelted. Recently, carbon-filled thermoplastic resins [e.g., polypropylene (PP), liquid-crystalline polymer, polyphenylene sulfide, and polyethylene] have been considered for fuel cell bipolar plates.^{19–23}

In this study, we performed compounding runs followed by the injection molding of carbon-filled PP resins. PP has been studied by several researchers for possible use in fuel cell bipolar plates.^{19,24} PP is a semicrystalline thermoplastic that can be remelted and used again. Three different carbon fillers [electrically conductive carbon black (CB), synthetic graphite (SG) particles, and carbon nanotubes (CNTs)] were studied. Composites containing various amounts of a single type of carbon filler were fabricated and tested for electrical conductivity. Composites containing combinations of the fillers were also investigated via a factorial design with a replicate. The goal of this project was to determine the effects and interactions of each filler on the composite electrical conductivity (1/electrical resistivity).

EXPERIMENTAL

Materials

The matrix used for this project was Dow's semicrystalline homopolymer PP resin H7012-35RN (Midland, MI). The properties of this polymer are shown in Table I.²⁵

The first filler used in this study was Ketjenblack EC-600 JD. This is an electrically conductive CB available from Akzo Nobel, Inc. (Chicago, IL) The highly branched, high-surface-area CB structure allows it to contact a large amount of polymer, which results in improved electrical conductivity at

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TABLE I
Properties of Dow's H7012-35RN PP Resin²⁵

Melting point	163°C
Glass-transition temperature	-6.6°C
Melt flow rate (230°C/2.16 kg)	35 g/10 min
Density	0.9 g/cc
Tensile strength at yield	34 MPa
Tensile elongation at yield	7%
Flexural modulus	1420 MPa
Notched Izod impact strength	25 J/m
Deflection temperature under load at 0.45 MPa, unannealed	110°C

low CB concentrations (often 5–7 wt %). The properties of Ketjenblack EC-600 JD are given in Table II.²⁶ The CB is in the form of pellets that are 100 μm to 2 mm in size and, upon mixing into a polymer, easily separate into primary aggregates 30–100 nm long.²⁶ Figure 1 shows a diagram of this CB structure.

Table III shows the properties of Thermocarb TC-300 from Asbury Carbons (Asbury, NJ), which is a primary SG previously sold by Conoco.^{27,28} Thermocarb TC-300 is produced from a thermally treated, highly aromatic petroleum feedstock and contains very few impurities. Figure 2 shows a photomicrograph of this SG.

Hyperion Catalysis International's FIBRIL nanotubes (Cambridge, MA) were the third filler used in this study. These are conductive, vapor-grown, multiwalled CNTs. They are produced from high-purity, low-molecular-weight hydrocarbons in a proprietary, continuous, gas-phase, catalyzed reaction. The outside diameter of the tube is 10 nm, and the length is 10 μm , which gives an aspect ratio (length/diameter) of 1000. Because of this high aspect ratio, very low concentrations of nanotubes are needed to produce an electrically conductive composite. This material was provided by Hyperion Catalysis International in a 20 wt % FIBRIL master batch, MB3020-01. Table IV shows the properties of this carbon filler.²⁹

The concentrations (shown in weight percentages and the corresponding volume percentages) for all of the single-filler composites tested in this research are shown in Table V. Increasing filler amount increased the composite melt viscosity. Because of

TABLE II
Properties of the Akzo Nobel Ketjenblack EC-600 JD²⁶

Electrical resistivity	0.01–0.1 $\Omega\text{ cm}$
Aggregate size	30–100 nm
Specific gravity	1.8 g/cm ³
Apparent bulk density	100–120 kg/m ³
Ash content maximum	0.1 wt %
Moisture maximum	0.5 wt %
Brunauer–Emmett–Teller surface area	1250 m ² /g
Pore volume	480–510 cm ³ /100 g



Figure 1 Structure of Ketjenblack EC-600 JD.

the large increase in composite melt viscosity, CB was used only at low loading levels.³⁰ The maximum single-filler content that could be extruded and injection-molded into test specimens were 15 wt % for CB, 80 wt % for SG, and 15 wt % for the CNTs.

Table VI shows the factorial design. For all fillers, the low loading level was 0 wt %. The high loading levels varied for each filler. The high loading levels were 2.5 wt % for Ketjenblack EC-600 JD CB, 65 wt % for Thermocarb TC-300 SG, and 6 wt % for FIBRIL CNTs. Because, in this project, we focused on producing highly conductive composites, the loading levels were chosen so that the filler amounts would produce conductive composites and still allow the composite material to have a low enough viscosity to be extruded and injection-molded into the test specimens. Table VII shows the weight percentage and the corresponding volume percentage for all of the factorial design formulations (original and replicate). Tables V and VII also show the

TABLE III
Properties of the Thermocarb TC-300 SG^{27,28}

Filler	Thermocarb TC-300 SG
Carbon content	99.91 wt %
Ash	<0.1 wt %
Sulfur	0.004 wt %
Density	2.24 g/cc
Brunauer–Emmett–Teller surface area	1.4 m ² /g
Thermal conductivity at 23°C	600 W/mK in crystallographic direction <i>a</i>
Electrical resistivity of bulk carbon powder at 150 psi and 23°C parallel to the pressing axis	0.020 $\Omega\text{ cm}$
Particle shape	Acicular
Particle aspect ratio	1.7
Sieve analysis	
+600 μm	0.19 wt %
+500 μm	0.36 wt %
+300 μm	5.24 wt %
+212 μm	12.04 wt %
+180 μm	8.25 wt %
+150 μm	12.44 wt %
+75 μm	34.89 wt %
+44 μm	16.17 wt %
-44 μm	10.42 wt %

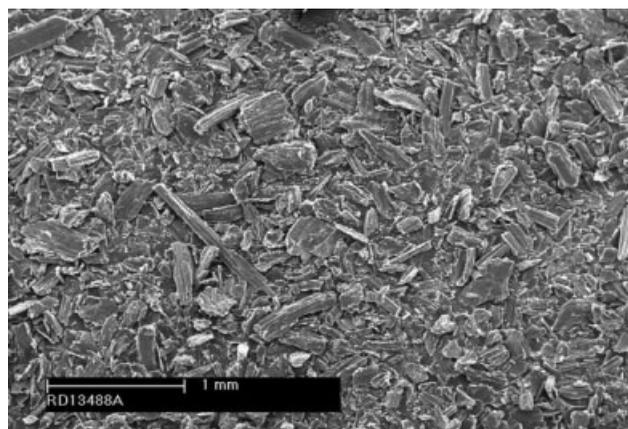


Figure 2 Photomicrograph of Thermocarb TC-300 SG (courtesy of Asbury Carbons).

electrical resistivity results that are described later in this article.

Test specimen fabrication

For this entire project, the fillers and PP were used as received. The extruder used was an American Leistritz Extruder Corp. (Somerville, NJ) model ZSE 27. This extruder had a 27-mm corotating intermeshing twin screw with 10 zones and a length/diameter ratio of 40. The screw design, which is shown elsewhere,³⁰ was chosen to obtain a minimum amount of filler degradation and still disperse the fillers well in the polymers. The pure PP pellets and the Hyperion FIBRIL masterbatch MB3020-01 (containing 20 wt % CNTs) were introduced in zone 1. For all of the composites containing single fillers, SG and CB were added to the polymer melt at zone 5. For the composites containing combinations of fillers, CB was added to the polymer melt at zone 7; SG was added to the polymer melt at zone 5. Fillers were added at two different zones to adequately mix the large amount of fillers. Schenck AccuRate gravimetric feeders (Whitewater, WI) were used to accurately control the amount of each material added to the extruder.

After passing through the extruder, the polymer strands (3 mm in diameter) entered a water bath and then a pelletizer that produced pellets nominally 3 mm long. After extrusion, the PP-based composites were dried in an indirectly heated dehumidifying drying oven at 80°C for 4 h and then stored in moisture-barrier bags before injection molding.

A Niigata injection molding machine (model NE85UA₄) (Tokyo, Japan) was used to produce test specimens. This machine had a 40-mm-diameter single screw with a length/diameter ratio of 18. The lengths of the feed, compression, and metering sections of the single screw were 396, 180, and 144 mm,

respectively. A four-cavity mold was used to produce 3.2 mm thick ASTM type I tensile bars (end gated) and 6.4-cm-diameter disks (end gated).

Through-plane electrical resistivity test method

For samples with an electrical resistivity greater than $10^4 \Omega \text{ cm}$, a through-plane (also called transverse) volumetric electrical conductivity test was conducted. In this method, a constant voltage (typically, 100 V) was applied to the as-molded test specimen, and the resistivity was measured according to ASTM D 257 with a Keithley 6517A electrometer/high-resistance meter and an 8009 resistivity test fixture.³¹ Keithley 6524 high-resistance measurement software (Cleveland, OH) was used to automate the conductivity measurement. For each formulation, a minimum of six specimens was tested. Each test specimen was an injection-molded disk that was 6.4 cm in diameter and 3.2 mm thick.

In-plane electrical resistivity test method

The volumetric in-plane (also called longitudinal) electrical resistivity was measured on all samples with an electrical resistivity lower than $10^4 \Omega \text{ cm}$. Test specimens cut from the center gauge portion of a tensile bar were surface-ground on all sides and then cut into sticks 2 mm wide by 2 mm thick by 25.4 mm long. Typically, for each formulation, a total of six specimens was cut from a single tensile bar, and three tensile bars were used to obtain a total of 18 test specimens.³² These samples were then tested with the four-probe technique. This technique measures resistivity by the application of a constant current (typically, 5–10 mA) and measurement of the voltage drop over the center 6 mm of the sample.³³ A Keithley 224 programmable current source and Keithley 182 digital sensitive voltmeter were used. Equation (1) was then used to calculate the electrical resistivity ($\Omega \text{ cm}$):

$$\text{Electrical resistivity} = \frac{\Delta V_{wt}}{iL} \quad (1)$$

TABLE IV
Properties of the FIBRIL CNTs²⁹

Composition	Pure carbon with a trace of residual metal oxide catalyst
Diameter	0.01 μm
Length	10 μm
Morphology	Typically, eight graphitic sheets wrapped around a hollow 0.005- μm core
Brunauer–Emmett–Teller (N ₂) surface area	250 m^2/g
Density	2.0 g/cc

TABLE V
Single-Filler Loading Levels in PP and Electrical Resistivity Results

Formulation	Filler		Electrical resistivity (Ω cm)
	wt %	vol %	
PP	0.0	0.0	$1.65 \times 10^{17} \pm 5.54 \times 10^{16}$, $n = 8$
PP replicate	0.0	0.0	$1.42 \times 10^{17} \pm 3.30 \times 10^{16}$, $n = 6$
2.5CB	2.5	1.27	$1.10 \times 10^{16} \pm 4.53 \times 10^{15}$, $n = 9$
2.5CB replicate	2.5	1.27	$1.31 \times 10^{16} \pm 3.93 \times 10^{15}$, $n = 6$
4CB	4.0	2.04	6811.72 ± 828.53 , $n = 5$
5CB	5.0	2.56	641.35 ± 50.96 , $n = 5$
6CB	6.0	3.09	192.30 ± 31.33 , $n = 5$
7.5CB	7.5	3.90	11.66 ± 0.43 , $n = 5$
10CB	10.0	5.26	2.93 ± 0.16 , $n = 26$
15CB	15.0	8.11	1.15 ± 0.03 , $n = 24$
10SG	10.0	4.27	$1.39 \times 10^{17} \pm 2.92 \times 10^{16}$, $n = 8$
15SG	15.0	6.62	$9.42 \times 10^{16} \pm 1.15 \times 10^{16}$, $n = 6$
20SG	20.0	9.13	$6.19 \times 10^{16} \pm 1.29 \times 10^{16}$, $n = 6$
25SG	25.0	11.81	$3.33 \times 10^{16} \pm 4.75 \times 10^{15}$, $n = 6$
30SG	30.0	14.69	$1.07 \times 10^8 \pm 2.72 \times 10^7$, $n = 6$
35SG	35.0	17.79	5484.40 ± 1411.30 , $n = 15$
40SG	40.0	21.13	394.12 ± 68.46 , $n = 19$
45SG	45.0	24.74	98.89 ± 11.11 , $n = 27$
50SG	50.0	28.66	39.18 ± 4.59 , $n = 22$
55SG	55.0	32.93	17.89 ± 2.61 , $n = 24$
60SG	60.0	37.60	8.40 ± 0.75 , $n = 21$
65SG	65.0	42.70	3.43 ± 0.68 , $n = 27$
65SG replicate	65.0	42.70	3.34 ± 0.73 , $n = 30$
70SG	70.0	48.40	1.31 ± 0.22 , $n = 29$
75SG	75.0	54.66	0.38 ± 0.06 , $n = 22$
80SG	80.0	61.64	0.09 ± 0.01 , $n = 20$
1.5CNT	1.5	0.68	$9.90 \times 10^{16} \pm 3.66 \times 10^{15}$, $n = 6$
2.5CNT	2.5	1.14	$1.36 \times 10^{16} \pm 5.02 \times 10^{15}$, $n = 9$
4CNT	4.0	1.84	$2.71 \times 10^{15} \pm 3.22 \times 10^{14}$, $n = 6$
5CNT	5.0	2.31	$5.22 \times 10^7 \pm 6.42 \times 10^7$, $n = 6$
6CNT	6.0	2.79	15.86 ± 1.65 , $n = 29$
6CNT replicate	6.0	2.79	18.29 ± 1.31 , $n = 29$
7.5CNT	7.5	3.52	5.09 ± 0.37 , $n = 29$
10CNT	10.0	4.76	1.56 ± 0.08 , $n = 30$
15CNT	15.0	7.36	0.40 ± 0.02 , $n = 30$

where ΔV is the voltage drop over the center 0.6 cm of the sample (V), w is the sample width (cm), t is the sample thickness (cm), i is the current (A), and L is the length over which ΔV is measured (0.6 cm).

Through-plane electrical resistivity (U.S. Fuel Cell Council) test method

The samples containing 4–7.5 wt % CB were out of range for both test methods described previously. For these samples, the transverse (through-plane) volumetric electrical resistivity of the 63.5-mm-diameter injection-molded disks were determined according to the U.S. Fuel Cell Council with a Keithley 2182A nanovoltmeter and a Keithley 2400 source meter.³⁴ For each formulation, typically, five samples were tested.

SG length, aspect ratio, and orientation test method

To determine the length and aspect ratio (length/diameter) of the SG in the injection-molded test speci-

mens, xylene at 120°C was used to dissolve the polymer matrix. The fillers were then dispersed onto a glass slide and viewed with an Olympus SZH10 optical microscope with an Optronics Engineering LX-750 video camera (Orangeburg, NY). The filler images (at 70 \times magnification) were collected with

TABLE VI
Filler Loading Levels in the Factorial Design Formulation

Formulation	Ketjenblack (wt %)	Thermocarb (wt %)	FIBRIL (wt %)
No filler	0	0	0
2.5CB	2.5	0	0
65SG	0	65	0
6CNT	0	0	6
2.5CB/65SG	2.5	65	0
2.5CB/6CNT	2.5	0	6
65SG/6CNT	0	65	6
2.5CB/65SG/6CNT	2.5	65	6

TABLE VII
Filler Loadings in the Factorial Design Formulations and
Electrical Resistivity Results

Formulation	Composition			Electrical resistivity (Ω cm)
	Constituent	wt %	vol %	
No filler (PP)				
Original	PP	100	100	$1.65 \times 10^{17} \pm 5.54 \times 10^{16}$, $n = 8$
Replicate				$1.42 \times 10^{17} \pm 3.30 \times 10^{16}$, $n = 6$
2.5CB				
Original	CB	2.5	1.3	$1.10 \times 10^{16} \pm 4.53 \times 10^{15}$, $n = 9$
Replicate	PP	97.5	98.7	$1.31 \times 10^{16} \pm 3.93 \times 10^{15}$, $n = 6$
65SG				
Original	SG	65	42.7	3.43 ± 0.68 , $n = 27$
Replicate	PP	35	57.3	3.34 ± 0.73 , $n = 30$
6CNT				
Original	CNT	6.0	2.8	15.86 ± 1.65 , $n = 29$
Replicate	PP	94.0	97.2	18.29 ± 1.31 , $n = 29$
2.5CB/65SG				
Original	CB	2.5	2.1	0.356 ± 0.026 , $n = 18$
Replicate	SG	65	43.6	0.358 ± 0.031 , $n = 15$
	PP	32.5	54.3	
2.5CB/6CNT				
Original	CB	2.5	1.3	2.19 ± 0.18 , $n = 26$
Replicate	CNT	6	2.8	2.16 ± 0.12 , $n = 27$
	PP	91.5	95.9	
65SG/6CNT				
Original	SG	65	45.2	0.0559 ± 0.0098 , $n = 16$
Replicate	CNT	6	4.7	0.0558 ± 0.0090 , $n = 33$
	PP	29	50.1	
2.5CB/65SG/6CNT				
Original	CB	2.5	2.2	0.0261 ± 0.004 , $n = 21$
Replicate	SG	65	46.2	0.0268 ± 0.004 , $n = 19$
	CNT	6	4.8	
	PP	26.5	46.8	

Scion Image version 1.62 software. The images were then processed with Adobe Photoshop 5.0 (San Jose, CA) and the Image Processing Tool Kit version 3.0 (Natick, MA). The length and aspect ratio of each particle was measured. For each formulation, approximately 1000 particles were measured.

To determine the orientation of the SG in the injection-molded test specimen, a polished composite sample was viewed with an optical microscope. For the through-plane electrical resistivity samples, the center portion was cut out of a disk and then mounted in epoxy so that the sample thickness (3.2 mm) through the face could be viewed. For the in-plane electrical resistivity samples, the samples were cast in epoxy so that the direction of flow induced during the injection-molding process, which was also the electrical resistivity measurement direction (lengthwise direction), would be viewed. The samples were then polished and viewed with an Olympus BX60 reflected light microscope at a magnification of 200 \times . The images were then processed with Adobe Photoshop 5.0 and the Image Processing Tool Kit version 3.0. For each formulation, we determined the orientation by viewing typically 1000 particles.

RESULTS

SG length, aspect ratio, and orientation results

The length and aspect ratio of the Thermocarb in the injection-molded specimens were typically 40 μ m and 1.67, respectively. These values were similar to those of the as-received material and those in prior studies of nylon, polycarbonate, and liquid-crystal polymer resins.³⁵⁻³⁷

Figure 3 illustrates that the SG particles, for the in-plane electrical resistivity samples, were primarily oriented in the in the measurement direction (lengthwise). The fillers in the through-plane samples were primarily oriented transverse to the electrical resistivity measurement direction. These observations agreed with prior work, and additional photomicrographs can be seen elsewhere.^{31,35,36,38,39}

Electrical resistivity results

Single fillers

The mean, standard deviation, and number of samples tested for each formulation containing various

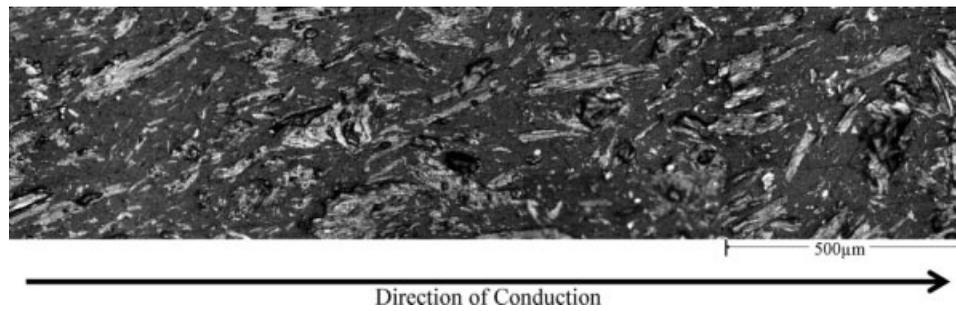


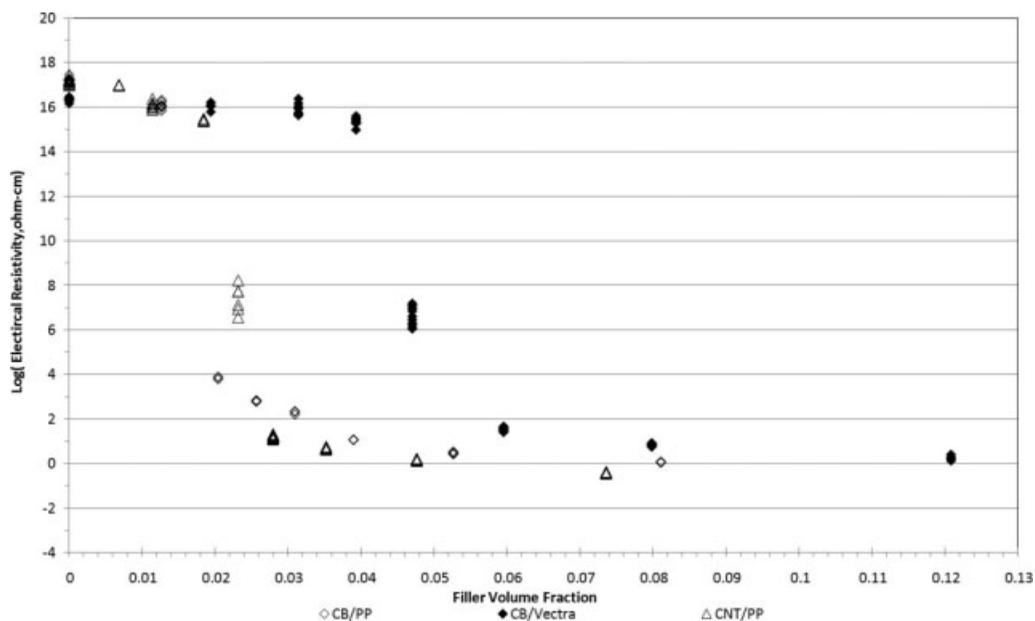
Figure 3 In-plane electrical resistivity sample containing 65 wt % Thermocarb TC-300 SG in PP at 200 \times magnification.

amounts of single fillers are shown in Table V. Figures 4 and 5 show the logarithm (electrical resistivity in Ω cm) for composites containing various amounts of single fillers as a function of filler volume fraction. In these figures, all the data points have been plotted. Figures 4 and 5 follow the typical electrical resistivity curve. At low filler loadings, the electrical resistivity remained similar to that of the pure polymer. Then, at a point called the *percolation threshold*, the resistivity decreased dramatically over a very narrow range of filler concentrations. At higher filler loadings, the electrical resistivity began to level out again at a value many orders of magnitude lower than that of the pure polymer.^{5,40}

Figure 4 illustrates that CB and CNTs were effective at decreasing the electrical resistivity (1/electrical conductivity) at low filler loadings. The pure PP had a mean electrical resistivity of 1.5×10^{17} Ω cm. The percolation threshold occurred at 1.4 vol % for CB and 2.1 vol % for CNTs. At the highest filler con-

centration, the CB produced a mean composite resistivity of 1 Ω cm (15 wt % = 8.1 vol %), compared to 0.4 Ω cm for the CNT composite (15 wt % = 7.4 vol %). The percolation threshold was likely low for the CB composites because of the highly branched, high-surface-area CB structure and for the CNT composites because of the filler high aspect ratio of 1000. These electrical resistivity results for CB in Ticona's Vectra A950 liquid-crystal polymer are also shown in Figure 4, which was previously reported by this research group.³⁷ For the CB/Vectra composites, the percolation threshold was 3.7 vol %, and the lowest electrical resistivity was 2 Ω cm (15 wt % = 12.1 vol %). Other researchers have noted that CB/PP composites often have a lower percolation threshold.^{12,26}

Figure 5 shows that the percolation threshold for the Thermocarb SG/PP composites occurred at 13 vol %. This higher filler amount needed for the percolation threshold for composites containing Thermocarb was due to the different particle shape/



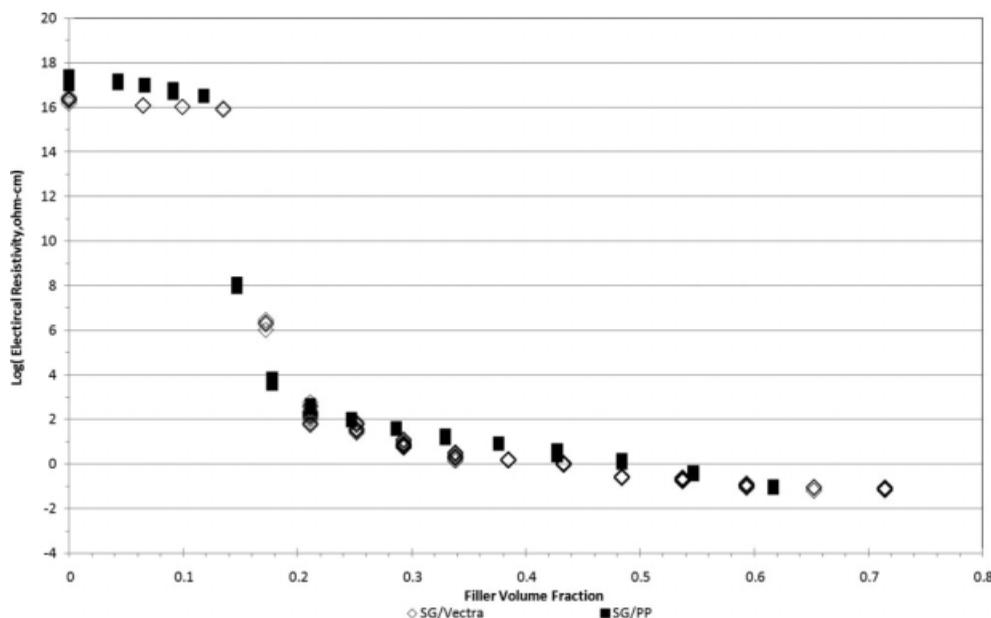


Figure 5 Single-filler electrical resistivity results for SG composites.

structure and properties of SG particles as compared to the CB and CNTs (see Tables II–IV). The Thermocarb had a much smaller aspect ratio (1.7) than CNTs (1000) and the highly branched CB structure. The Thermocarb also had a much smaller surface area of $1.4 \text{ m}^2/\text{g}$, as compared to $1250 \text{ m}^2/\text{g}$ for CB and $250 \text{ m}^2/\text{g}$ for CNTs. The composites containing 80 wt % (61.6 vol %) Thermocarb had a mean electrical resistivity of $0.09 \text{ } \Omega \text{ cm}$. Figure 5 also shows for the Thermocarb SG/Vectra composites, the percolation threshold was 15 vol %, and the lowest electrical resistivity for the 80 wt % (71.4 vol %) composite was $0.08 \text{ } \Omega \text{ cm}$.³⁷

Factorial design analysis

Table VII shows the mean, standard deviation, and number of specimens tested for the factorial design formulations (original and replicate). With these results, an analysis of the factorial design was conducted with the logarithm (mean electrical resistivity, $\Omega \text{ cm}$) as the response. This analysis was performed with the Minitab version 13 statistical software package. For this analysis, the effects and P (sometimes designated as p) values for the electrical resistivity results were calculated. Small p values indicate that a factor (filler in this case) may have had a significant effect on the composite electrical resistivity.⁴¹ For all statistical calculations, the 95% confidence level was used.

Factorial designs were used in the project because they were the most efficient type of experiment to determine the effect of each filler and any possible interactions between fillers. By using factorials, one can determine the effect that each factor (filler) has

on the system by calculating a single value to quantify the change in electrical resistivity as the weight percentage of a filler is increased. These calculated effects can then be ranked to determine which fillers and combinations of fillers produce a larger change.⁴¹

The effects and P values are given in Table VIII, which shows the values for all of the filler combinations. Further investigation of Table VIII yields some important information regarding the effects that the fillers had on electrical resistivity. For the composites containing only single fillers, SG, followed by CNTs, and then CB, caused a statistically significant decrease (negative effect term) in the composite electrical resistivity ($P < 0.05$). SG caused the largest decrease in electrical resistivity (largest effect term), followed closely by the CNTs. SG likely caused the largest decrease in electrical resistivity because it was added at the highest filler amount (65 wt % = 42.7 vol %). The CNTs were added at 6 wt % (2.79 vol %), and these composites had almost as much of a reduction in electrical resistivity, likely because of

TABLE VIII
Factorial Design Analysis for the Logarithm of the Electrical Resistivity ($\Omega \text{ cm}$)

Term	Effect	P
Constant		0.000
2.5CB	-0.825	0.000
65SG	-9.396	0.000
6CNT	-8.652	0.000
2.5CB/65SG	0.174	0.000
2.5CB/6CNT	0.216	0.000
65SG/6CNT	7.196	0.000
2.5CB/65SG/6CNT	0.110	0.000

the high aspect ratio (1000), high surface area (250 m²/g), and conductive networks that CNTs are known to form.²⁹ The composites containing 2.5 wt % (1.27 vol %) CB likely had the lowest reduction in electrical resistivity because of the small amount of CB used.

All of the combinations of different fillers had a statistically significant effect on electrical resistivity ($P < 0.05$). In every case, the effect term was positive, which means that the composite electrical resistivity increased when these two or three different fillers were used together. For example, when SG and CNTs were combined into a composite, the composite electrical resistivity was higher than what would be expected from the additive effect of each single filler.⁴¹ This statistically significant effect and positive effect term for different carbon fillers has been noted previously in nylon 6,6 based resins³² and Vectra-based resins.³⁷

Table VII shows that the electrical resistivity for the composite containing 2.5 wt % CB, 65 wt % SG, and 6 wt % CNTs (designated 2.5CB/65SG/6CNT) in PP was 0.0264 Ω cm, which corresponded to an electrical conductivity (1/electrical resistivity) of 38 S/cm. The U.S. Department of Energy electrical conductivity target for bipolar plates is 100 S/cm.²² Other researchers have shown that composites produced by compression molding, as opposed to injection molding, have produced materials with higher electrical conductivity.⁴² Hence, this three-filler combination (2.5CB/65SG/6CNT in PP) was compression-molded at 6.9 MPa at 230°C and tested. The mean electrical resistivity of these composites was 0.011 Ω cm (standard deviation = 0.0009 Ω cm for 34 samples tested), which gave an electrical conductivity result of 91 S/cm. This was near the target value. The higher electrical conductivity for compression molding, as compared to injection molding, was likely because the fillers were more oriented in the in-plane direction of measurement, which was induced in the manufacturing process. Hence, further optimization of this CB/SG/CNT/PP material system will be the subject of future studies and could achieve the electrical conductivity goal for bipolar plates.

CONCLUSIONS

The object of this research was to determine the effects and interactions of each filler on composite electrical resistivity. For the composites containing single fillers, the percolation threshold was 1.4 vol % for the CB/PP composites, 2.1 vol % for the CNT/PP composites, and 13 vol % for the SG/PP composites. Hence, small amounts of CB and CNTs needed to be added to dramatically reduce the composite electrical resistivity. The lowest electrical resistivity

for the composites containing single fillers was 1 Ω cm for 15 wt % CB/PP, 0.4 Ω cm for 15 wt % CNT/PP, and 0.09 Ω cm for 80 wt % SG/PP.

Several observations were made from the electrical resistivity factorial design analysis. First, for the composites containing only single fillers, SG, followed closely by CNTs, and then CB, caused a statistically significant decrease (negative effect term) in the composite electrical resistivity. Thus, the addition of these single fillers to PP caused a statistically significant decrease in composite electrical resistivity. Second, all of the composites containing combinations of different fillers showed a statistically significant effect on electrical resistivity. This effect term was positive, which meant that the composite electrical resistivity was higher than what would be expected from the additive effect of the single fillers.

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