

# Electrical Conductivity Modeling of Carbon-Filled Liquid-Crystalline Polymer Composites

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**ABSTRACT:** Electrically conductive resins are needed for bipolar plates used in fuel cells. Currently, the materials for these bipolar plates often contain a single type of graphite powder in a thermosetting resin. In this study, various amounts of two different types of carbon, carbon black and synthetic graphite, were added to a thermoplastic matrix. The resulting single-filler composites were tested for electrical conductivity, and electrical conductivity models were developed. Two different models, the Mamunya and additive electrical conductivity models, were used for both material systems. It was determined how to modify these models to reduce the number of ad-

justable parameters. The models agreed very well with experimental data covering a large range of filler volume fractions (from 0 to 12 vol % for the carbon black filled composites and from 0 to 65 vol % for the synthetic graphite filled composites) and electrical conductivities (from  $4.6 \times 10^{-17}$  S/cm for the pure polymer to 0.5 S/cm for the carbon black filled composites and to 12 S/cm for the synthetic graphite filled composites). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3293–3300, 2006

**Key words:** composites; fillers; liquid-crystalline polymers (LCP)

## 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 bipolar plates for use in fuel cells. A bipolar plate separates one cell from the next, carrying hydrogen gas on one side and air (oxygen) on the other side. Bipolar plates require high thermal and electrical conductivity (to conduct heat and to minimize ohmic losses), low gas permeability, and good dimensional stability.

Electrical conductivity values (S/cm) are typically  $10^{-14}$  to  $10^{-17}$  for polymers,  $10^2$  for carbon black,  $10^5$  for high-purity synthetic graphite, and  $10^6$  for metals such as aluminum and copper. One approach to improving the electrical conductivity of a polymer is the addition of a conductive filler material, such as carbon or metal.<sup>1–14</sup> Currently, a single type of graphite powder is typically used in thermosetting resins (often a vinyl ester) to produce a thermally and electrically conductive bipolar-plate material.<sup>15–18</sup> Thermosetting resins cannot be remelted.

Conductive resins can be used for many different applications. Conductive resins with electrical conductivity ranging from approximately  $10^{-10}$  to  $10^{-3}$  S/cm can be used for static dissipative applications. Those with an electrical conductivity from approximately  $10^{-2}$  to  $10^{-1}$  S/cm can be used for semiconducting applications (e.g., fuel gauges). Conductive resins with an electrical conductivity of 10 S/cm or more can be used for electromagnetic-interference/radio-frequency-interference applications.<sup>14</sup> For bipolar-plate applications, the desired electrical conductivity is greater than 50 S/cm.<sup>19–21</sup>

In this work, researchers performed compounding runs followed by the injection molding of carbon-filled Vectra A950RX. Vectra is a thermoplastic that can be remelted and used again. One carbon black and one synthetic graphite were used as fillers. Material characterization tests included the volumetric electrical resistivity. The goal of this project was to determine how various amounts of these single carbon fillers affected the composite electrical conductivity and to develop improved electrical conductivity models for these composites.

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## EXPERIMENTAL

### Materials

The matrix used for this project was Vectra A950RX liquid-crystalline polymer (Ticona, Summit, NJ), which

**TABLE I**  
Properties of Vectra A950RX from Ticona

Melting point	280°C
Tensile modulus (1 mm/min)	10.6 GPa
Tensile stress at break (5 mm/min)	182 MPa
Tensile strain at break (5 mm/min)	3.4%
Flexural modulus at 23°C	9.1 GPa
Notched Izod impact strength at 23°C	95 KJ/m <sup>2</sup>
Density at 23°C	1.40 g/cc
Volumetric electrical conductivity at 23°C	10 <sup>-15</sup> S/cm
Surface electrical conductivity	10 <sup>-14</sup> S
Thermal conductivity at 23°C	≈ 0.2 W/mK
Humidity absorption (23°C/50% relative humidity)	0.03 wt %
Mold shrinkage: parallel	0.0%
Mold shrinkage: normal	0.7%
Coefficient of linear thermal expansion: parallel	0.04 × 10 <sup>-4</sup> /°C
Coefficient of linear thermal expansion: normal	0.38 × 10 <sup>-4</sup> /°C

The data were taken from ref. 22.

is a highly ordered, thermoplastic copolymer consisting of 73 mol % hydroxybenzoic acid and 27 mol % hydroxynaphtholic acid. This liquid-crystalline polymer has the properties needed for bipolar plates, namely, high dimensional stability up to 250°C, extremely short molding times (often 5–10 s), exceptional dimensional reproducibility, chemical resistance to the acidic environments present in fuel cells, and a low hydrogen gas permeation rate.<sup>22,23</sup> The properties of this polymer are shown in Table I.<sup>22</sup>

The first filler used in this study was Ketjenblack EC-600 JD. This is an electrically conductive carbon black available from Akzo Nobel, Inc. (Chicago, IL). The highly branched, high-surface-area carbon black structure allows it to contact a large amount of the polymer, and this results in improved electrical conductivity at low carbon black concentrations (often 5–7 wt %). The properties of Ketjenblack EC-600 JD are given in Table II.<sup>24</sup> The carbon black is in the form of pellets that are 100 μm to 2 mm in size and, upon mixing with a polymer, easily separate into primary aggregates 30–100 nm long.<sup>24</sup> Figure 1 shows a diagram of this carbon black structure.<sup>24</sup>

Table III shows the properties of Thermocarb TC-300 (Asbury Carbons, Asbury, NJ), which is a pri-

**TABLE II**  
Properties of Ketjenblack EC-600 JD from Akzo Nobel

Electrical conductivity	10–100 S/cm
Aggregate size	30–100 nm
Specific gravity	1.8 g/cm <sup>3</sup>
Apparent bulk density	100–120 kg/m <sup>3</sup>
Ash content (maximum)	0.1 wt %
Moisture (maximum)	0.5 wt %
Brunauer–Emmett–Teller surface area	1250 m <sup>2</sup> /g
Pore volume	480–510 cm <sup>3</sup> /100 g

The data were taken from ref. 24.



**Figure 1** Structure of Ketjenblack EC-600 JD primary aggregate.

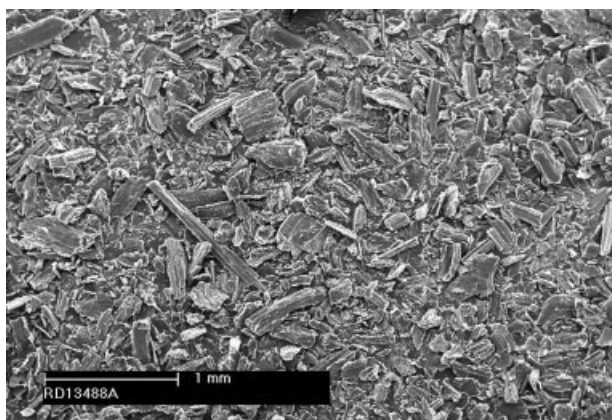
mary synthetic graphite that was previously sold by Conoco.<sup>25,26</sup> Thermocarb TC-300 is produced from a thermally treated, highly aromatic petroleum feedstock and contains very few impurities. Figure 2 shows a photomicrograph of this synthetic graphite.<sup>25</sup>

The electrical conductivity was measured on composites containing various amounts of these carbon fillers in Vectra A950RX. The concentrations (shown as weight percentages and the corresponding volume percentages) for these single-filler composites are shown in Tables IV and V. Prior work with nylon 6,6 and polycarbonate has shown that the concentrations selected for these fillers will yield electrically

**TABLE III**  
Properties of Thermocarb TC-300 Synthetic Graphite

Filler	Thermocarb TC-300 synthetic graphite
Carbon	99.91 wt %
Ash	< 0.1 wt %
Sulfur	0.004 wt %
Density	2.24 g/cc
Brunauer–Emmett–Teller surface area	1.4 m <sup>2</sup> /g
Thermal conductivity at 23°C	600 W/mK in the "a" crystallographic direction
Electrical conductivity of the bulk carbon powder at 150 psi and 23°C: parallel to the pressing axis	50 S/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 %

The data were taken from refs. 25 and 26.



**Figure 2** Photomicrograph of Thermocarb TC-300 synthetic graphite.<sup>25</sup>

conductive resins.<sup>27,28</sup> For bipolar-plate applications, typically 60–70 wt % synthetic graphite is used.<sup>15</sup>

### Test specimen fabrication

For this entire project, the fillers were used as received. Vectra A950RX was dried in an indirectly heated, dehumidifying, drying oven at 150°C and then stored in moisture-barrier bags.

The extruder was an American Leistritz Extruder Corp. model ZSE 27 (Somerville, NJ). This extruder had a 27-mm, corotating, intermeshing twin screw with 10 zones and a length/diameter ratio of 40. The screw design used has been shown elsewhere.<sup>29</sup> The screw design was chosen to allow a large concentration of the filler to mix with the matrix material and thereby achieve the maximum possible conductivity. The Vectra polymer pellets were introduced in zone 1. A side stuffer located at zone 5 was used to introduce the carbon fillers into the polymer melt. Two Schenck AccuRate (Whitewater, WI) gravimetric feeders 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 nominally 3-mm-long pellets. After compounding, the pelletized

**TABLE IV**  
Single-Filler-Loading Levels of Ketjenblack EC-600 JD in Vectra

Filler (wt %)	Filler (vol %)
0.0	0.0
2.5	1.9
4.0	3.1
5.0	3.9
6.0	4.7
7.5	6.0
10.0	8.0
15.0	12.1

**TABLE V**  
Single-Filler-Loading Levels of Thermocarb TC-300 in Vectra

Filler (wt %)	Filler (vol %)
0.0	0.0
10.0	6.5
15.0	9.9
20.0	13.5
25.0	17.2
30.0	21.1
35.0	25.2
40.0	29.3
45.0	33.8
50.0	38.5
55.0	43.3
60.0	48.4
65.0	53.7
70.0	59.3
75.0	65.2

composite resin was dried again and then stored in moisture-barrier bags before injection molding.

A Niigata model NE85UA<sub>4</sub> injection-molding machine (Tokyo, Japan) was used to produce the 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.

The temperature profile typically used was 280°C in zone 1 (nearest the feed hopper), 307°C in zones 2 and 3, and 315°C in zone 4. 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). The electrical conductivity values of all formulations were determined. Before the electrical conductivity tests were conducted, the samples were conditioned at 23°C and 50% relative humidity for 88 h.<sup>30</sup>

### Through-plane electrical conductivity test method

For samples with an electrical conductivity less than 10<sup>-4</sup> S/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.<sup>31</sup> Keithley 6524 high-resistance measurement software was used to automate the conductivity measurements (Cleveland, OH). For each formulation, at least six specimens were tested. Each test specimen was an injection-molded disk that was 6.4 cm in diameter and 3.2 mm thick.

### In-plane electrical conductivity test method

The volumetric in-plane (also called longitudinal) electrical conductivity was measured for all samples

with an electrical conductivity greater than  $10^{-4}$  S/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 6 specimens were cut from a single tensile bar, and three tensile bars were typically used to obtain a total of 18 test specimens.<sup>32</sup> These samples were then tested with the four-probe technique. This technique measures the conductivity by applying a constant current (typically 5–10 mA) and measuring the voltage drop over the center 6 mm of the sample.<sup>8</sup> A Keithley 224 programmable current source and a Keithley 182 digital sensitive voltmeter were used. Equation (1) was then used to calculate the electrical conductivity:

$$EC = \frac{(i)(L)}{(\Delta V)(w)(t)} \quad (1)$$

where  $EC$  is the electrical conductivity (S/cm),  $\Delta V$  is the voltage drop over the center 0.6 cm of 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  $\Delta V$  is measured (0.6 cm).

### Filler orientation test method

Because of the small size of the carbon black (the primary aggregates were 30–100 nm), the carbon black filler orientation was not measured. To determine the orientation of the synthetic graphite, a polished composite sample was viewed with an optical microscope. For each formulation, an in-plane electrical conductivity sample was cast in epoxy so that the direction of flow induced during the injection-molding process, which was also the direction of electrical conductivity measurement (lengthwise direction), would be viewed. For the through-plane electrical conductivity samples, the center portion was cut out of a disk and set in epoxy so that the through-the-sample-thickness (3.2 mm) face could be viewed. The samples were then polished and viewed with an Olympus BX60 reflected light microscope (Melville, NY) at a magnification of 100 or 200 $\times$ . The images were then processed with Adobe Photoshop 5.0 (San Jose, CA) and Image Processing Tool Kit (version 3.0) (Ashville, NC). For each formulation, the orientation was typically determined from 1000–2000 particles.

## RESULTS

### Filler orientation results

As discussed previously, the filler orientation angle ( $\theta$ ) was measured by optical microscopy. The angle of interest was the deviation of the filler away from

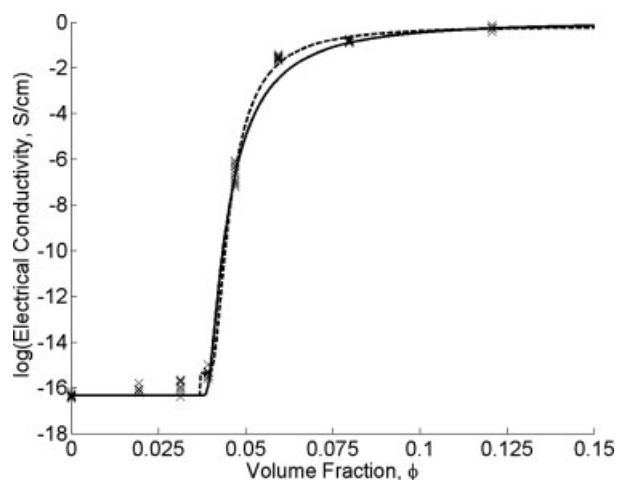
the direction of the conductivity measurement. All the angles were between 0 and 90°. An angle of 0° signified that the fillers were aligned parallel to the measurement direction. An angle of 90° meant that the fillers were perpendicular (transverse) to the measurement direction.

For the in-plane electrical conductivity sample containing 60 wt % Thermocarb TC-300 synthetic graphite in Vectra A950RX, the mean orientation angle was 24°, which indicated that most of the fillers were oriented in the electrical conductivity measurement direction. This photomicrograph has been shown elsewhere.<sup>33</sup> This result is typical for all the samples in this study, and it agrees with previous work.<sup>32</sup>

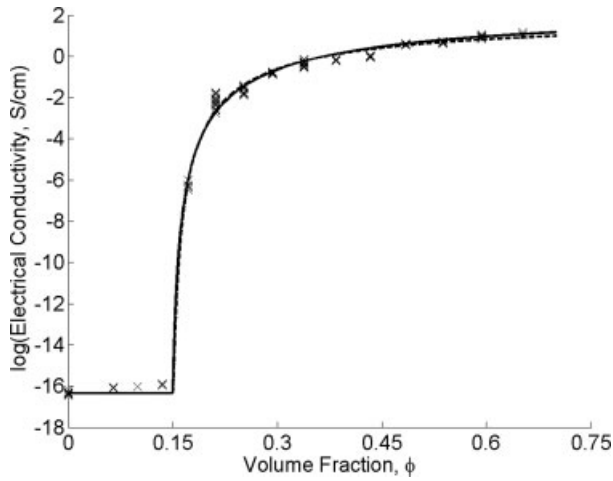
For the through-plane electrical conductivity samples, the mean orientation angle was typically 52°, which indicated that the fillers were primarily oriented transversely to the conductivity measurement direction. This observation agrees with previous work.<sup>34</sup> A photomicrograph of a sample containing 70 wt % Thermocarb TC-300 synthetic graphite in Vectra A950RX has been shown elsewhere.<sup>29</sup>

### Electrical conductivity results

Figures 3 and 4 show the logarithm of the electrical conductivity (S/cm) for composites containing various amounts of single fillers as a function of the filler volume fraction ( $\phi$ ). All the data points have been plotted. These figures follow the typical electrical conductivity curve. At low filler loadings, the electrical conductivity remains similar to that of the pure polymer. Then, at a point called the percolation threshold ( $\phi_c$ ), the conductivity increases dramatically over a very narrow range of filler concentra-



**Figure 3** Electrical conductivity results for Vectra A950RX/Ketjenblack EC-600 JD composites. The symbols are the experimental data points, the solid line is the Mamunya model, and the dashed line is the additive model.



**Figure 4** Electrical conductivity results for Vectra A950RX/Thermocarb TC-300 composites. The symbols are the experimental data points, the solid line is the Mamunya model, and the dashed line is the additive model.

tions. At higher filler loadings, the electrical conductivity begins to level out again at a value many orders of magnitude higher than that of the pure polymer.<sup>5,35</sup>

Figure 3 shows that carbon black is effective at increasing the electrical conductivity at low filler loadings. The pure Vectra A950RX has a mean electrical conductivity of  $4.6 \times 10^{-17}$  S/cm (the vendor literature states  $10^{-15}$  S/cm).<sup>22</sup>  $\phi_c$  for carbon black is 3.7 vol %. At the highest filler concentration, the carbon black produced a mean composite conductivity of 0.5 S/cm (15 wt % = 12.1 vol %). These electrical conductivity results are similar to those reported elsewhere.<sup>5,24</sup>

Figure 4 shows that  $\phi_c$  for Thermocarb synthetic graphite occurs at 15 vol %. This higher filler amount needed for  $\phi_c$  for composites containing Thermocarb is due to the different particle shape/structure and properties of synthetic graphite particles versus carbon black (see Figs. 1 and 2 and Tables II and III). The composites containing 60 and 70 wt % (48.4 and 59.3 vol %) Thermocarb had mean electrical conductivities of 3.8 and 9.1 S/cm, respectively.

### Electrical conductivity modeling results

In this section, we present two separate model results for the electrical conductivity of carbon/liquid-crystalline polymer composites. The first is the thermodynamic model of Mamunya and coworkers,<sup>36,37</sup> and the second is an additive equation recently developed by Clingerman et al.<sup>28</sup> A detailed review of the electrical conductivity and percolation theory models for composite materials has been presented by Lux.<sup>38</sup>

### Modified Mamunya model

Mamunya and coworkers<sup>36,37</sup> developed a model in which the electrical conductivity of a composite [ $\sigma$  (S/cm)] is a function of the deviation of  $\phi$  from  $\phi_c$ . This model (modified by Clingerman et al.<sup>28</sup>) also depends on the filler and polymer surface energy ( $\gamma_{pf}$ ) and is given by eqs. (2)–(5):

$$\log(\sigma) = \log(\sigma_p) + [\log(\sigma_F) - \log(\sigma_p)] \left( \frac{\phi - \phi_c}{F - \phi_c} \right)^k \quad (2)$$

where  $\sigma_p$  is the electrical conductivity of the pure polymer (S/cm) and is assumed to be equivalent to the composite electrical conductivity up to and including  $\phi_c$ . Furthermore,  $\sigma_F$  is the electrical conductivity (S/cm) at maximum packing volume fraction  $F$ , which is the maximum volume fraction at which electrical conductivity data are obtained. Hence,  $\sigma_F$  corresponds to the composite with the highest electrical conductivity. Thus, this model depends on at least two experimentally measured data points ( $\sigma_p$  at  $\phi_c$  and  $\sigma_F$  at  $F$ ), so the model is exact at these two data points. For  $\phi \leq \phi_c$ ,  $\sigma$  is equal to  $\sigma_p$ . The exponent  $k$  in eq. (2) is calculated as follows:

$$k = \frac{K\phi_c}{(\phi - \phi_c)^n} \quad (3)$$

Factor  $K$  is described by

$$K = A - B\gamma_{pf} \quad (4)$$

This model contains three adjustable parameters:  $A$ ,  $B$ , and  $n$ . This model also depends on  $\gamma_{pf}$ . Clingerman et al.<sup>28</sup> used the Fowkes equation,<sup>39</sup> modified by Owens and Wendt,<sup>40</sup> to obtain  $\gamma_{pf}$ :

$$\gamma_{pf} = \gamma_p + \gamma_f - 2(\gamma_p^d \gamma_f^d)^{0.5} - 2(\gamma_p^p \gamma_f^p)^{0.5} \quad (5)$$

where  $\gamma_p^d$  is the dispersive component of the polymer surface tension,  $\gamma_p^p$  is the polar component of the polymer surface tension, and  $\gamma_p$  is the total polymer surface tension (the sum of the polar and dispersive components). Similarly,  $\gamma_f^d$  is the dispersive component of the filler surface tension,  $\gamma_f^p$  is the polar component of the filler surface tension, and  $\gamma_f$  is the total filler surface tension (the sum of the polar and dispersive components). The values for all these factors are listed in Table VI,<sup>41</sup> and the test methods used are described elsewhere.<sup>28</sup>

The results of the Mamunya model [eqs. (2)–(5)] are shown in Figure 3 for Ketjenblack EC-600 JD/

TABLE VI  
Surface Tension Properties for the Mamunya Electrical Conductivity Model

Material	Polar component of the surface energy (mJ/m <sup>2</sup> )	Dispersive component of the surface energy (mJ/m <sup>2</sup> )	Total surface energy (mJ/m <sup>2</sup> )
Vectra A950 RX	6.87	29.25	36.12
Ketjenblack EC-600 JD	2.18	19.59	21.77
Thermocarb TC-300	3.99	20.01	24.00

The data were taken from ref. 41.

Vectra A950 RX composites and in Figure 4 for Thermocarb TC-300/Vectra A950RX composites. To generate the Mamunya model curves in Figure 3, the adjustable parameters chosen for the carbon black/Vectra composites are  $A = -1.90$  (dimensionless),  $B = 0.87 \text{ m}^2/\text{mJ}$ , and  $n = 0.96$  (dimensionless), with  $\phi_c = 0.037$  (dimensionless),  $\sigma_p = 4.57 \times 10^{-17} \text{ S/cm}$ ,  $F = 0.121$  (dimensionless), and  $\sigma_F = 0.537 \text{ S/cm}$ . It is also noted that  $\gamma_{pf} = 2.275 \text{ mJ/m}^2$  and  $K = 0.079$  (dimensionless). In Figure 4, for the synthetic graphite/Vectra composites, the parameters  $A = 0.20$  (dimensionless),  $B = 0.082 \text{ m}^2/\text{mJ}$ , and  $n = 0.34$  (dimensionless) are used with  $\phi_c = 0.15$  (dimensionless),  $\sigma_p = 4.57 \times 10^{-17} \text{ S/cm}$ ,  $F = 0.65$  (dimensionless), and  $\sigma_F = 11.95 \text{ S/cm}$ . It is also noted that  $\gamma_{pf} = 1.263 \text{ mJ/m}^2$  and  $K = 0.30$  (dimensionless). As a final note, the dependence of the Mamunya model on the surface tension effects can be eliminated; this reduces the model to two adjustable, dimensionless parameters:  $n$  and  $K$ . For this reason, we report the  $K$  values in the previous discussion.

#### Additive model

Clingerman et al.<sup>28</sup> developed an additive model that is meant to capture the effects of the percolation phenomena, structure, and surface energy. For  $\phi \leq \phi_c$ ,  $\sigma$  is equal to  $\sigma_p$ . For  $\phi > \phi_c$ , the additive model is given by eqs. (6)–(8):

$$\log(\sigma) = \log(\sigma_p) + D \log(\sigma_F)(\phi - \phi_c)^k + f(\text{structure}) + f(\text{surface energy}) \quad (6)$$

where  $D$  is an arbitrary constant. Again,  $\sigma_F$  corresponds to the electrical conductivity at maximum packing volume fraction  $F$ . The value of  $k$  is given by

$$k = \frac{K\phi_c}{(\phi - \phi_c)^n} \quad (7)$$

The structure relationship is given as  $f(\text{structure}) = h(a) \cos \theta$ , where  $\theta$  is filler orientation angle and  $h(a)$  is a function of the aspect ratio of the filler ( $a$ ).<sup>42</sup> Note that  $1 < a < \infty$ :

$$h(a) = A^2 \left\{ 1 - \frac{1}{2} \left[ A - \frac{1}{A} \right] \ln \left[ \frac{A+1}{A-1} \right] \right\} \quad (8)$$

where  $A^2$  is equal to  $a^2/(a^2 - 1)$ . Finally, the surface energy relationship is given as  $f(\text{surface energy}) = -C\gamma_{pf}$ , where  $C$  is an adjustable parameter.

In this article, we simplify the additive model given in eqs. (6)–(8). The aspect ratio is constant for each filler. The orientation of the filler was also shown to be constant. Thus,  $h(a) \cos \theta$  is a constant. The surface energy relationship equation multiplies a constant by surface tension  $\gamma_{pf}$  (which is also a constant). Thus, the structure and surface energy terms can be combined into one arbitrary parameter, which we assign to the variable  $E$ .

Looking at eq. (6), we find that  $\sigma_F$  is multiplied by arbitrary constant  $D$ . Furthermore, eq. (7) shows that  $\phi_c$  is multiplied by arbitrary constant  $K$ . These relationships can thus be simplified in terms of two new arbitrary parameters, which we assign to variables  $G$  and  $H$ . Thus, eqs. (6)–(8) can be rewritten in a simplified additive model:

$$\log(\sigma) = \log(\sigma_p) + H(\phi - \phi_c)^{G/(\phi - \phi_c)^n} + E \quad (9)$$

This depends on four adjustable parameters:  $E$ ,  $G$ ,  $H$ , and  $n$ .

To generate the additive model curves in Figure 3, the adjustable parameters chosen for the carbon black/Vectra composites are  $E = 0.97$  [units of  $\log(\text{S/cm})$ ],  $G = 4.8 \times 10^{-5}$  (dimensionless),  $H = 15.2$  [units of  $\log(\text{S/cm})$ ], and  $n = 1.7$  (dimensionless), with  $\phi_c = 0.037$  (dimensionless) and  $\sigma_p = 4.57 \times 10^{-17} \text{ (S/cm)}$ . In Figure 4, for the synthetic graphite/Vectra composites, the parameters are  $E = 0.0$  [units of  $\log(\text{S/cm})$ ],  $G = 2.7 \times 10^{-2}$  (dimensionless),  $H = 17.7$  [units of  $\log(\text{S/cm})$ ], and  $n = 0.44$  (dimensionless), with  $\phi_c = 0.15$  (dimensionless) and  $\sigma_p = 4.57 \times 10^{-17} \text{ (S/cm)}$ . There appears to be slightly better agreement with the new additive model [eq. (9)] than with the updated Mamunya model [eqs. (2)–(5)] for carbon black/Vectra composites. The agreement of both models

seems to be very good for synthetic graphite/Vectra composites.

Figure 3 shows that there is a small, secondary plateau near  $\phi_c$ . This is because the additive model has a discontinuity in the value of  $\log \sigma$  at  $\phi_c$  at a value of  $\log \sigma_p + E$ . Both the additive and Mamunya models have discontinuities in the slope at  $\phi_c$ . One can restrict the values of  $E$  to give a better fit but with increased deviation between the model and experimental results. In Figure 3, the value of  $E$  is acceptable because the logarithm of the experimental electrical resistivity at  $\phi = 0.0393$  (the first data set above  $\phi_c$ ) ranges from 15.0 to 15.6. For the data shown in Figure 4, the fit is better for negative values of  $E$ . This is an unrealistic result of this curve-fitting model, so we restrict  $E > 0$  and obtain the optimum solution at  $E = 0$ .

The crux of the most successful electrical conductivity models (e.g., those presented here) is the use of  $\sigma_p$  (for  $\phi < \phi_c$ ) and  $\sigma_f$ . The functional form chosen to describe the data between these extremes has no physical significance and may vary from the usual  $(\phi - \phi_c)^{C/(\phi - \phi_c)^n}$  to possibly give a better fit with less adjustable parameters. This will be addressed in a future article.

## CONCLUSIONS

In this project, two different electrical conductivity models were developed for liquid-crystalline polymer composites containing various amounts of either Ketjenblack EC-600 JD carbon black or Thermocarb TC-300 synthetic graphite particles. The Mamunya model showed very good agreement with the experimental data for the carbon black composites and excellent agreement for the synthetic graphite composites. The additive model showed excellent agreement for both sets of composites tested here.

These models cover a wide range of experimental data. For carbon black composites, the model accurately estimated the electrical conductivity for the pure polymer ( $4.6 \times 10^{-17}$  S/cm) through  $\phi_c$  (3.7 vol %) and up to the maximum loading of 12.1 vol % (with an electrical conductivity of 0.5 S/cm). For synthetic graphite composites, the model estimated the electrical conductivity behavior of the pure polymer through  $\phi_c$  (15 vol %) and up to the maximum loading of 65.2 vol % (with an electrical conductivity of 12 S/cm).

The Mamunya model contains three adjustable parameters (although it is shown how it can be reduced to two adjustable parameters). The additive model has been modified to use four adjustable parameters. This higher number of adjustable parameters is likely the reason that the additive model better fits the experi-

mental data. Future work will explore the use of alternative electrical conductivity models.

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