Synergistic Effects of Carbon Fillers on Tensile and Flexural Properties in Liquid-Crystal Polymer Based Resins

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ABSTRACT: One emerging market for thermally and electrically conductive resins is bipolar plates for use in fuel cells. Adding carbon fillers to thermoplastic resins increases the composite thermal and electrical conductivity. These fillers have an effect on the composite tensile and flexural properties, which are also important for bipolar plates. In this study, various amounts of three different types of carbon (carbon black, synthetic graphite particles, and carbon fibers) were added to Vectra A950RX liquid-crystal polymer. In addition, composites containing combinations of fillers were also investigated via a factorial design. The tensile and flexural properties of the resulting composites were then measured. The objective of this study was to determine the effects and interactions of each filler with respect to the tensile and flexural properties. The addition of carbon black caused the tensile and flexural properties to decrease. Adding synthetic graphite particles caused the tensile and flexural modulus to increase. The addition of carbon fiber caused the tensile and flexural modulus and ultimate flexural strength to increase. In many cases, combining two different fillers caused a statistically significant effect on composite tensile and flexural properties at the 95% confidence level. For example, when 40 wt % synthetic graphite particles and 4 wt % carbon black were combined, the composite ultimate tensile and flexural strength increased more than what would be expected from the individual additive effect of each single filler. It is possible that linkages were formed between the carbon black and synthetic graphite particles that resulted in improved ultimate tensile and flexural strength. J Appl Polym Sci 108: 1657–1666, 2008

Key words: composites; fillers; liquid-crystalline polymers (LCP); mechanical properties; tension

INTRODUCTION

Most polymer resins are electrically and thermally insulating. Increasing the conductivity of these resins allows them to be used in other applications. One emerging market for electrically and thermally conductive resins is 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 conductivity (to conduct heat and to minimize ohmic losses), low gas permeability, good dimensional stability, and moderate tensile and flexural properties. The U.S. Department of Energy has set a target flexural strength for bipolar plates of 25 MPa.[1] PlugPower has set a desired flexural strength of greater than 59 MPa and a desired tensile strength of greater than 41 MPa.[2]

One approach to improving the electrical and thermal conductivity of a polymer is the addition of a conductive filler material, such as carbon or metal.[3–16] Currently, a single type of graphite powder (often 60 wt %) is typically used in thermosetting resins (often a vinyl ester) to produce a thermally and electrically conductive bipolar plate material.[17–20] Thermosetting resins cannot be remelted.

The addition of conductive fillers can degrade the mechanical properties of the conductive composite. Hence, these mechanical properties cannot be ignored. Thongruang et al.[21] investigated the electrical conductivity and mechanical properties of composites containing both graphite particles and carbon fiber in high-density polyethylene and ultrahigh-molecular-weight polyethylene.

In this work, researchers performed compounding runs followed by injection molding and mechanical testing of carbon/Vectra A950RX composites. Vectra

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TABLE I
Properties of Ticona's Vectra A950RX

Melting point	280°C
Tensile modulus (1 mm/min)	10.6 GPa
Tensile strength at break (5 mm/min)	182 MPa
Tensile strain at break (5 mm/min)	3.4%
Flexural modulus at 23°C	9.1 GPa
Flexural strength at 23°C	158.0 MPa
Notched Izod impact strength at 23°C	95 kJ/m^2
Density at 23°C	1.40 g/cc
Volumetric electrical resistivity at 23°C	10^{15} Ω cm
Surface electrical resistivity	10^{14} Ω
Thermal conductivity at 23°C	0.2 W/mK (approximately)
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^{-4}/°C
Coefficient of linear thermal expansion: normal	0.38×10^{-4}/°C

The data were taken from ref. 22.

is a liquid-crystal polymer thermoplastic that can be remelted and used again. Three different carbon fillers (electrically conductive carbon black, synthetic graphite particles, and carbon fibers) were studied. Composites containing various amounts of a single type of carbon filler were fabricated and tested. In addition, composites containing combinations of 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 with respect to the composite tensile and flexural properties.

EXPERIMENTAL

Materials

The matrix used for this project was Vectra A950RX liquid-crystal polymer (Ticona), which is a highly ordered thermoplastic copolymer consisting of 73 mol % hydroxybenzoic acid and 27 mol % hydroxynaphthoic acid. This liquid-crystal polymer has the properties needed for bipolar plates, that is, high dimensional stability up to a temperature of 250°C, extremely short molding times (often 5–10 s), exceptional dimensional reproducibility, chemical resistance in the acidic environments present in a fuel cell, and a low hydrogen gas permeation rate.[22,23] The properties of this polymer are shown in Table I.[22]

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 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.[24] The carbon black 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.[24] Figure 1 shows a diagram of this carbon black structure.

TABLE II
Properties of Akzo Nobel Ketjenblack EC-600 JD

Electrical resistivity	0.01–0.1 Ω 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

The data were taken from ref. 24.

Table III shows the properties of Thermocarb TC-300 (Asbury Carbons, Asbury, NJ), which is a primary synthetic graphite that was previously sold by Conoco.[25,26] 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.

Fortafil 243 carbon fiber, sold by Toho Tenax America, Inc., was the third filler used in this study. Fortafil 243 (Rockwood, TN) is a polyacrylonitrile-based, 3.2-mm chopped and pelletized carbon fiber that is often used to improve the electrical and thermal conductivity and tensile and flexural properties of resins. Fortafil 243 is surface-treated and then formed into pellets by the manufacturer. A proprietary polymer (sizing) is used as a binder for the pellets that also promotes adhesion with the matrix. Table IV shows the properties of this carbon fiber.[27]

The concentrations (shown as weight percentages and the corresponding volume percentages) for all of the single-filler composites tested in this research are shown in Table V. Increasing the filler amount increases the composite melt viscosity. Because of the large increase in the composite melt viscosity, carbon black is used only at low loading levels.[28] The maximum single-filler contents that could be extruded and injection-molded were 10 wt % for

Figure 1 Structure of Ketjenblack EC-600 JD.

TABLE III
Properties of Thermocarb TC-300 Synthetic Graphite

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

The data were taken from refs. 25 and 26.

carbon black, 60 wt % for synthetic graphite, and 45 wt % for carbon fiber. Table VI shows the factorial design formulations. For all fillers, the low loading level was 0 wt %. The high loading levels varied for each filler. The high loading levels were 4 wt % for Ketjenblack EC-600 JD carbon black, 40 wt % for Thermocarb TC-300 synthetic graphite, and 10 wt % for Fortafil 243 carbon fiber. Because this project focuses on producing highly conductive composites, the loading levels were chosen so that the filler

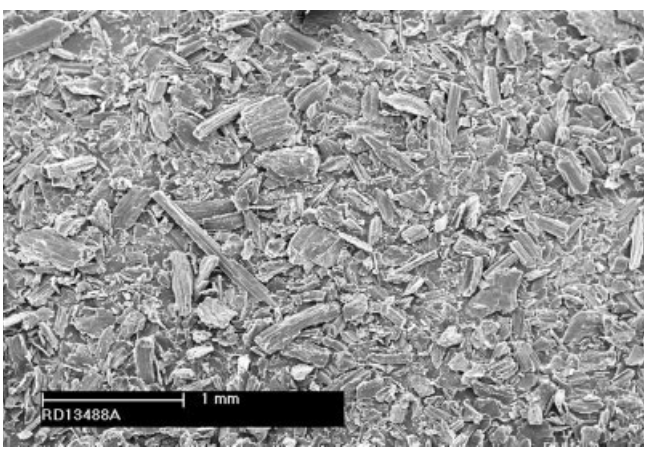

Figure 2 Photomicrograph of Thermocarb TC-300 synthetic graphite. (Courtesy of Asbury Carbons)

TABLE IV
Properties of Fortafil 243 Carbon Fiber

Carbon content	95 wt %
Electrical resistivity	0.00167 Ω cm
Thermal conductivity	20 W/mK (axial direction)
Tensile strength	3800 MPa
Tensile modulus	227 GPa
Specific gravity	1.74 g/cc
Fiber diameter	7.3 μm
Fiber shape	Round
Fiber mean length	3.2 mm (entire range = 2.3–4.1 mm)
Binder content	2.6 wt % proprietary polymer that adheres pellets together and promotes adhesion with the nylon matrix
Bulk density	356 g/L

The data were taken from ref. 27.

amounts would produce conductive composites while still allowing the composite material to have a low enough viscosity to be extruded and injection-molded into test specimens. In the tables, CB is used to signify carbon black (Ketjenblack EC-600JD), SG is used for synthetic graphite (Thermocarb TC-300), and CF is used for carbon fiber (Fortafil 243). Because of the high viscosity of the resin, the composite containing all three fillers (carbon black, synthetic graphite, and carbon fiber) could not be extruded and injection-molded into test specimens.

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 used was an American Leistritz Extruder Corp. (Somerville, NJ) model ZSE 27. This ex-

TABLE V
Single Filler Loading Levels

Filler (wt %)	Ketjenblack (vol %)	Thermocarb (vol %)	Fortafil (vol %)
2.5	1.9	N/A	N/A
4.0	3.1	N/A	N/A
5.0	3.9	N/A	4.1
6.0	4.7	N/A	N/A
7.5	6.0	N/A	6.1
10.0	8.0	6.5	8.2
15.0	N/A	9.9	12.4
20.0	N/A	13.5	16.8
25.0	N/A	17.2	21.2
30.0	N/A	21.1	25.5
35.0	N/A	25.2	30.2
40.0	N/A	29.3	34.9
45.0	N/A	33.8	39.7
50.0	N/A	38.5	N/A
55.0	N/A	43.3	N/A
60.0	N/A	48.4	N/A

N/A = not applicable.

TABLE VI
Filler Loading Levels in Factorial Design Formulations

Formulation	Ketjenblack (wt %)	Thermocarb (wt %)	Fortafil (wt %)
No filler	0	0	0
CB	4	0	0
SG	0	40	0
CB*SG	4	40	0
CF	0	0	10
CB*CF	4	0	10
SG*CF	0	40	10

truder has a 27-mm corotating, intermeshing twin screw with 10 zones and a length/diameter ratio of 40. The screw design has been shown elsewhere.[28] It was chosen to allow a large concentration of filler to mix with the matrix material and thereby achieve the maximum possible tensile, flexural, and conductive properties. The polymer pellets (Vectra) were introduced in zone 1. For all the composites containing single fillers, the fillers were added to the polymer melt at zone 5. For the composites containing combinations of fillers, carbon fiber was added to the polymer melt at zone 7; carbon black and synthetic graphite were added to the polymer melt at zone 5. Schenck (Whitewater, WI) AccuRate 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 composite resin was dried again and then stored in moisture-barrier bags before injection molding.

A Niigata (Tokyo, Japan) model $NE85UA_4$ injection-molding machine was used to produce test specimens. This machine has 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 are 396, 180, and 144 mm, respectively.

The temperature profile typically used was 280°C in zone 1 (nearest 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 127-mm-long, 12.7-mm-wide flexural bars (end-gated). The tensile and flexural properties of all formulations were determined. Before the tests were conducted, the samples were conditioned at 23°C and 50% relative humidity for 88 h, and then they were tested.[29]

Filler length, aspect ratio, and orientation test method

To determine the length and aspect ratio of the carbon fiber and synthetic graphite in the test specimens, diethylenetriamine was used to dissolve the matrix. The fillers were then dispersed onto a glass slide and viewed with an Olympus (Orangeburg, NY) SZH10 optical microscope with an Optronics (Goleta, CA) Engineering LX-750 video camera. The filler images (at 70× magnification) were collected with Scion Image version 1.62 software. The images were then processed with Adobe Photoshop 5.0 and Image Processing Tool Kit version 3.0. The length and aspect ratio of each filler were measured. For each formulation, 1000–6000 particles/fibers were measured. Because of the extremely small size of the carbon black, the length and aspect ratio of the carbon black were not measured.

To determine the orientation of the carbon fillers, a polished composite sample was viewed with an optical microscope. Again, because of the small size of the carbon black (aggregates 30–100 nm in size), the orientation of only the synthetic graphite particles and carbon fibers was determined. One 25 mm × 2 mm piece was cut from the center of a tensile specimen. This sample was cast in a two-part epoxy plug so that the direction of flow induced during the injection-molding process, which was also the direction of tensile testing, could be viewed. The sample was then polished and viewed with an Olympus BX60 reflected light microscope at a magnification of 200×. The images were then processed with Adobe Photoshop 5.0 and Image Processing Tool Kit version 3.0. For each formulation, the orientation was determined by the viewing of typically 1000–2000 particles/fibers.

Tensile test method

The tensile properties (at ambient conditions, 16.5-cm-long, 3.2-mm-thick ASTM type I sample geometry) from all formulations were determined with ASTM D 638 at a crosshead rate of 5 mm/min for reinforced plastics.[30] An Instru-Met (Union, NJ) Sintech screw-driven mechanical testing machine was used. The tensile modulus was calculated from the initial linear portion of the stress–strain curve. For each formulation, at least five samples were tested.

Flexural test method

The flexural properties were determined with three-point loading under ambient conditions from all formulations according to ASTM D 790 at a crosshead rate of 5.3 mm/min.[31] Each rectangular sample was 3.2 mm thick, 127.0 mm long, and 12.7 mm wide. A span of 102.4 mm (corresponding to a 32:1 span/thickness ratio) was used in an Instru-Met Sintech screw-driven mechanical testing machine. Deflection was measured with a linear variable displacement transducer. The flexural modulus was calculated from the initial linear portion of the load–deflection

curve. For each formulation, at least five samples were tested.

RESULTS

Filler length, aspect ratio, and orientation results

The length and aspect ratio of the Thermocarb in the molded composite samples were typically 50 μm and 1.68, respectively. These values are similar to those of the as-received material and prior work.[32,33] For the molded composites containing carbon fibers, the length was typically 70 μm. The corresponding fiber aspect ratio (length/diameter) was 9. These results agree with prior work.[32,33]

Figure 3 displays a photomicrograph of a tensile specimen containing 40 wt % Thermocarb TC-300, 10 wt % Fortafil 243, and 50 wt % Vectra A950RX at a magnification of 200×. The arrow under the figure indicates the tensile measurement direction, which is also the direction of flow (lengthwise) into the mold. This photomicrograph is typical of all the samples tested. As can be seen, the fillers are primarily aligned in the tensile test direction. These results agree with prior work.[32,33] Because both the tensile and flexural specimens are end-gated, the fillers in the flexural specimens are also primarily aligned in the lengthwise direction of the flexural bar.

Tensile test results

Figures 4–6 show the tensile results (tensile modulus, ultimate tensile strength, and strain at ultimate tensile strength) as the mean plus or minus the standard deviation for composites containing various amounts of single fillers as function of the filler volume percentage. These formulations correspond to those shown in Table V. If the standard deviation is smaller than the marker size, the error bars are not shown. In all cases, there was no observed necking in the samples tested. Hence, for each formulation, the ultimate (peak) tensile strength was nearly identical to the strength at fracture.

It is noted that the tensile modulus, ultimate tensile strength, and strain at ultimate tensile strength

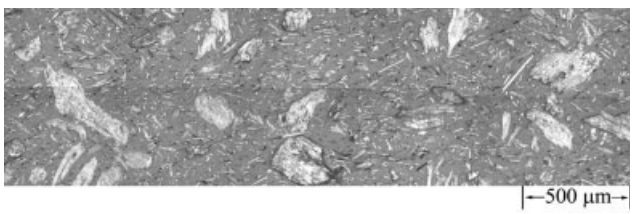

Figure 3 Photomicrograph of a 40 wt % Thermocarb TC-300 synthetic graphite/10 wt % Fortafil 243 carbon fiber/50 wt % Vectra A950RX tensile specimen at a magnification of 200×.

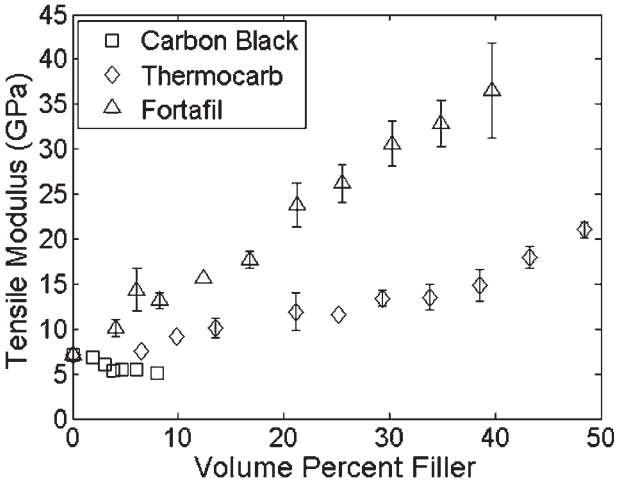

Figure 4 Tensile modulus for composites containing various amounts of single fillers.

for the neat Vectra were measured to be 7.1 GPa, 145 MPa, and 5.8%, respectively. These values are within 30% of those reported by the vendor literature (Table I). Differences are likely due to test specimen manufacturing methods.

The tensile modulus results for composites filled only with various amounts of the single fillers are located in Figure 4. Several observations can be made from Figure 4. First, adding carbon black caused the tensile modulus to decrease from 7.1 (neat polymer) to 5.1 GPa at 8 vol % (10 wt %) carbon black. Carbon black was used in this project primarily to increase the composite electrical conductivity. Second, adding synthetic graphite particles caused the tensile modulus to increase from 7.1 (neat polymer) to 21.0 GPa for the composite containing 48.4 vol % (60 wt %) Thermocarb. Adding Fortafil 243 carbon fiber allowed the tensile modulus to increase from 7.1 to 36.5 GPa for the composite containing 39.7 vol % (45 wt %) carbon fiber. The higher tensile modulus for the Fortafil carbon fiber/Vectra composites versus the Thermocarb/Vectra composites is likely due to the higher filler aspect ratio of 9 for the carbon fiber/Vectra composites versus 1.68 for synthetic graphite particle/Vectra composites.

Figure 5 illustrates the ultimate tensile strength results for composites filled only with various amounts of the single fillers. The addition of any of the fillers caused the composite ultimate tensile strength to decrease, with carbon black causing the steepest decline. Composites containing 8.0 vol % (10 wt %) carbon black had an ultimate tensile strength of 68.4 MPa versus 145 MPa for the neat polymer. Carbon fiber caused the smallest decline in the ultimate tensile strength. The composites containing 39.7 vol % (45 wt %) carbon fiber had an ultimate tensile strength of 123 MPa.

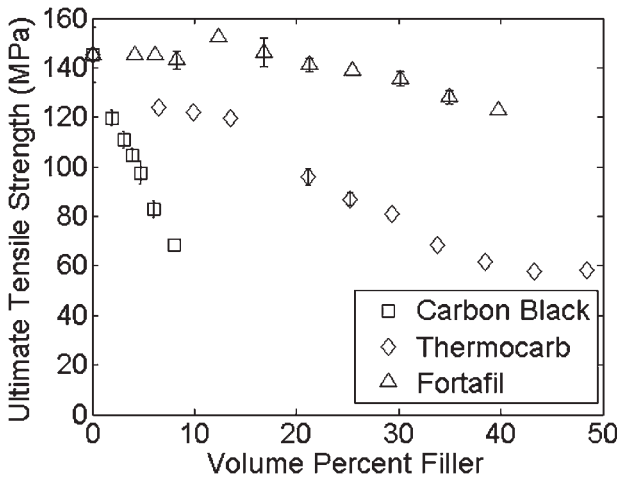

Figure 5 Ultimate tensile strength for composites containing various amounts of single fillers.

Figure 6 illustrates the strain at ultimate tensile strength results for composites filled only with various amounts of the single fillers. Once again, adding any of these fillers caused the strain at ultimate tensile strength to decrease. Again, carbon black caused the steepest decline. The composites containing 8.0 vol % (10 wt %) carbon black had a strain at ultimate tensile strength of 2.5% versus 5.8% for the neat polymer. Composites containing 60 wt % Thermocarb and 40 wt % Vectra A950RX and composites containing 45 wt % Fortafil carbon fiber and 55 wt % Vectra A950RX had a strain at ultimate tensile strength of 0.7%.

Flexural test results

Figures 7 and 8 show the flexural modulus and ultimate flexural strength as the mean plus or minus the standard deviation for composites containing various amounts of single fillers as function of the filler volume fraction. These formulations correspond to those shown in Table V. If the standard deviation is smaller than the marker size, the error bars are not shown.

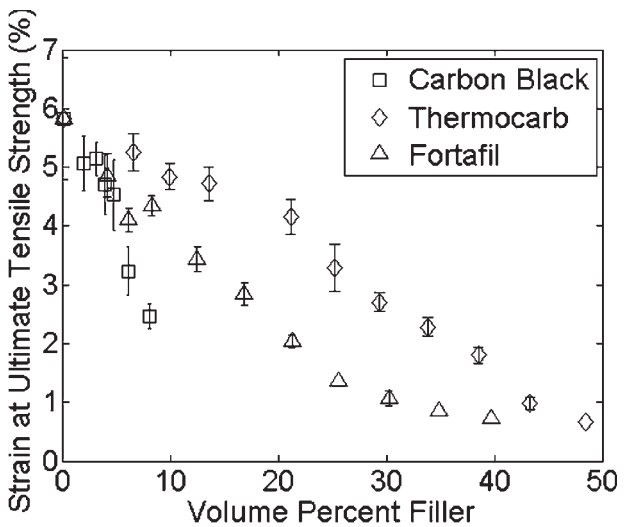

Figure 6 Strain at ultimate tensile strength for composites containing various amounts of single fillers.

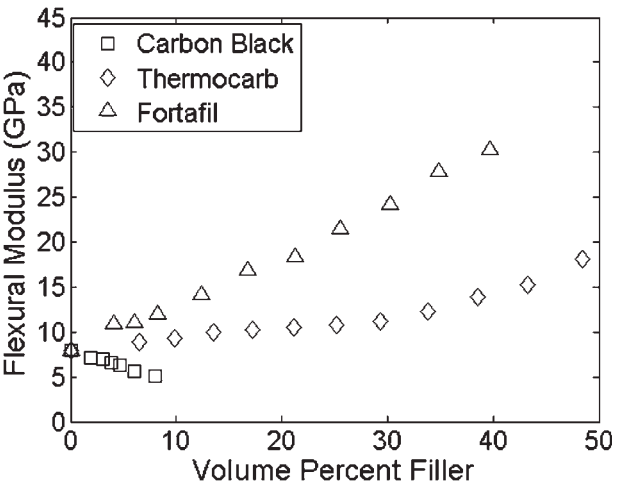

Figure 7 Flexural modulus for composites containing various amounts of single fillers.

Figure 7 shows the flexural modulus for composites containing various amounts of single fillers. Figures 4 (tensile modulus) and 7 (flexural modulus) show the same general trends. Adding carbon black caused the flexural modulus to decrease from 7.9 (neat polymer) to 5.1 GPa at 8 vol % (10 wt %) carbon black. Second, adding synthetic graphite particles caused the tensile modulus to increase from 7.9 (neat polymer) to 18.1 GPa for the composite containing 48.4 vol % (60 wt %) Thermocarb. Adding Fortafil 243 carbon fiber allowed the tensile modulus to increase from 7.9 to 30.3 GPa for the composite containing 39.7 vol % (45 wt %) carbon fiber. The higher flexural modulus for the Fortafil carbon fiber/Vectra

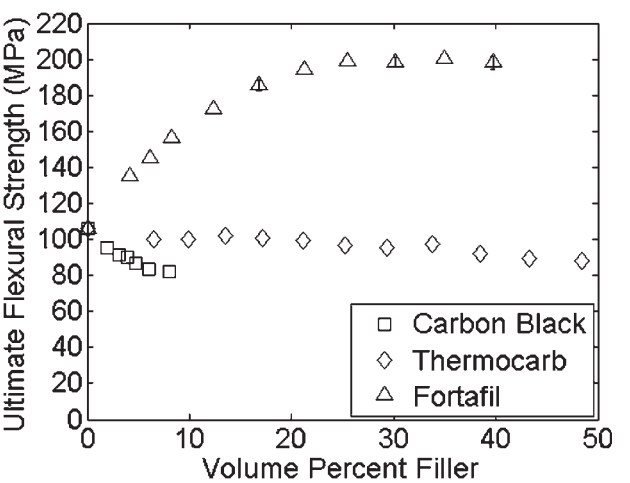

Figure 8 Ultimate flexural strength for composites containing various amounts of single fillers.

TABLE VII
Tensile Modulus for Factorial Design Formulations

Formulation	Tensile modulus (MPa)	
	Original	Replicate
No filler	7,080 ± 490, n = 7	7,060 ± 860, n = 6
CB	5,780 ± 460, n = 5	6,050 ± 620, n = 6
SG	13,970 ± 390, n = 5	12,920 ± 840, n = 6
CF	13,290 ± 870, n = 5	12,940 ± 870, n = 6
CB*SG	11,050 ± 530, n = 9	10,990 ± 540, n = 10
CB*CF	10,700 ± 490, n = 10	11,120 ± 680, n = 10
SG*CF	16,610 ± 290, n = 7	16,850 ± 540, n = 8

composites versus the Thermocarb/Vectra composites is likely due to the higher filler aspect ratio of 9 for the carbon fiber/Vectra composites versus 1.68 for the synthetic graphite particle/Vectra composites.

Figure 8 shows the flexural strength for composites containing various amounts of single fillers. The addition of carbon black caused the composite ultimate flexural strength to decrease from 106 MPa for the neat polymer to 82.0 MPa with 8.0 vol % (10 wt %) carbon black. Adding Thermocarb caused a gradual decline in the ultimate flexural strength, which decreased from 106 MPa for the neat polymer to 88.3 MPa for the composite with 48.4 vol % (60 wt %) Thermocarb. Carbon fiber caused the ultimate flexural strength to increase from 106 MPa for the neat polymer to 200 MPa for the composite with 39.7 vol % (45 wt %) carbon fiber. The higher ultimate flexural strength for the Fortafil carbon fiber/Vectra composites is likely due to the higher filler aspect ratio for the carbon fiber/Vectra composites.

It is noted that the flexural modulus and ultimate flexural strength for the neat Vectra were measured to be 7.9 GPa and 106 MPa, respectively. These values are within 30% of those reported by the vendor literature (Table I). Again, differences are likely due to test specimen manufacturing methods.

FACTORIAL DESIGN ANALYSIS

Tables VII–IX show the tensile modulus, ultimate strength, and strain at ultimate strength for the factorial design formulations. Tables X and XI show the flexural modulus and ultimate strength for the factorial design formulations. With the results shown in Tables VII–XI, an analysis of the factorial design was completed. This was performed with the Minitab Release 13 Statistical Software package. For this analysis, the effects and the T (also often designated t) and P (also often designated p) values for the results were calculated. Large T values and low P values indicate that the factor being studied (e.g., carbon fiber) has a significant effect on the property (e.g., tensile modulus) being investigated.[34] For all statistical calculations, the 95% confidence level was used.

Factorial designs were used in the project because they are 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 the tensile/flexural properties as the weight percentage of a filler is increased. These calculated effects can then be ranked to determine which fillers and combinations of fillers produced a larger change.

TABLE VIII
Ultimate Tensile Strength for Factorial Design Formulations

Formulation	Ultimate tensile strength (MPa)	
	Original	Replicate
No filler	144.1 ± 15.2, n = 7	146.4 ± 3.3, n = 6
CB	113.2 ± 3.4, n = 6	108.6 ± 1.0, n = 6
SG	81.1 ± 1.4, n = 7	80.6 ± 1.6, n = 7
CF	146.3 ± 2.6, n = 6	140.0 ± 0.8, n = 6
CB*SG	58.9 ± 1.3, n = 9	58.8 ± 0.4, n = 10
CB*CF	122.1 ± 1.2, n = 10	123.2 ± 1.6, n = 10
SG*CF	72.0 ± 0.4, n = 7	72.2 ± 1.3, n = 8

TABLE IX
Strain at Ultimate Tensile Strength for Factorial Design Formulations

Formulation	Strain at ultimate tensile strength (%)	
	Original	Replicate
No filler	5.6 ± 1.4, n = 7	6.0 ± 0.5, n = 6
CB	5.1 ± 0.3, n = 6	5.2 ± 0.3, n = 6
SG	2.8 ± 0.2, n = 7	2.6 ± 0.3, n = 7
CF	4.3 ± 0.2, n = 6	4.4 ± 0.1, n = 6
CB*SG	1.3 ± 0.2, n = 9	1.3 ± 0.1, n = 10
CB*CF	3.1 ± 0.3, n = 10	3.1 ± 0.3, n = 10
SG*CF	1.2 ± 0.1, n = 7	1.1 ± 0.1, n = 8

Tensile results

The effects and the T and P values for the tensile modulus are given in Table XII, which shows the values for all of the filler combinations. Further investigation of Table XII yields some important

TABLE X
Flexural Modulus for Factorial Design Formulations

Formulation	Flexural modulus (GPa)	
	Original	Replicate
No filler	7,930 ± 80, n = 5	7,920 ± 170, n = 5
CB	7,010 ± 60, n = 9	6,880 ± 140, n = 6
SG	12,000 ± 200, n = 5	11,020 ± 240, n = 5
CF	12,050 ± 250, n = 6	12,140 ± 170, n = 8
CB*SG	10,510 ± 180, n = 7	10,420 ± 180, n = 7
CB*CF	10,580 ± 140, n = 7	10,540 ± 100, n = 8
SG*CF	15,540 ± 110, n = 5	15,190 ± 160, n = 6

TABLE XI
Ultimate Flexural Strength for Factorial Design Formulations

Formulation	Flexural strength (MPa)	
	Original	Replicate
No filler	105.8 ± 1.2, n = 6	106.3 ± 1.2, n = 5
CB	94.0 ± 1.4, n = 6	91.5 ± 0.7, n = 5
SG	98.7 ± 1.3, n = 5	95.1 ± 0.2, n = 5
CF	156.4 ± 2.0, n = 7	153.2 ± 1.5, n = 5
CB*SG	97.3 ± 1.0, n = 8	96.1 ± 0.9, n = 7
CB*CF	142.6 ± 0.5, n = 6	141.1 ± 0.4, n = 5
SG*CF	116.3 ± 0.8, n = 7	114.9 ± 0.7, n = 7

information regarding the effects that single fillers and combinations of fillers have on the tensile modulus. The addition of any of the single fillers had a statistically significant effect on the tensile modulus at the 95% confidence level ($P < 0.05$). The addition of 40 wt % synthetic graphite particles caused the largest increase (largest and positive effect term) in the tensile modulus. This was followed closely by the addition of 10 wt % carbon fiber, which also caused a statistically significant increase in the tensile modulus. The addition of 4 wt % carbon black caused a statistically significant decrease (negative effect term) in the tensile modulus. Two of the two-filler combinations (synthetic graphite particle/carbon fiber and carbon black/synthetic graphite particles) also had a statistically significant and negative effect (negative effect terms) on the tensile modulus ($P < 0.05$). For these composites containing combinations of two different fillers, the largest effect was for the 40 wt % synthetic graphite particles and 10 wt % carbon fiber composite, followed by the 4 wt % carbon black and 40 wt % synthetic graphite composite. The two-filler combination of carbon black and carbon fiber did not have a statistically significant effect ($P > 0.05$). The statistically significant results for two of the two-way interactions show that there is an effect on the tensile modulus when different fillers are combined. In this case, a statistically significant interaction term indicates that the composite tensile modulus is lower than what would be expected from the additive effect of each single filler.[34] This means that, for example, when 40 wt % synthetic graphite and 10 wt % carbon fiber were combined, the tensile modulus of the composite decreased more than what would be expected from the individual additive effects of synthetic graphite and carbon fiber.

Table XIII shows the effects and the T and P values for the ultimate tensile strength, showing the values for all of the filler combinations. Of all the single fillers, the addition of 40 wt % synthetic graphite particles and 4 wt % carbon black caused a statistically significant decrease in the ultimate tensile strength (negative effect term). The addition of 40 wt % synthetic graphite had the largest effect on the ultimate tensile strength. Adding 10 wt % carbon fiber did not have a statistically significant effect on the ultimate tensile strength ($P > 0.05$). For the composites containing two different fillers, the composites containing carbon black and carbon fiber caused a statistically significant and positive effect on the ultimate tensile strength. This was followed closely by the composite containing both carbon black and synthetic graphite. The composite containing both synthetic graphite particles and carbon fiber did not have a statistically significant effect on the ultimate tensile strength ($P > 0.05$). The statistically significant results for two of the two-way interactions shown in Table XIII indicate that there is an effect on the ultimate tensile strength when different fillers are combined. For example, the most significant combination was that of carbon black and carbon fiber. This means that, for example, when carbon black and carbon fiber were combined, then the ultimate tensile strength of the composite was higher than what would be expected from the additive effect of each single filler.[34]

The effects and the T and P values for the strain at ultimate tensile strength are given in Table XIV, which shows the values for all of the filler combinations. For all the single fillers, all the effect terms are negative, and this indicates that the addition of any filler reduced the composite tensile strain. The addition of any of these single fillers caused a statistically significant decrease in the tensile strain ($P < 0.05$), with the synthetic graphite particles having the largest effect, followed by carbon fiber and then carbon black. For the composites containing two different

TABLE XII
Factorial Design Analysis for Tensile Modulus (MPa)

Term	Effect	T	P
Constant		97.64	0.000
CB	−2314	−9.88	0.000
SG	4363	18.63	0.000
CF	4141	17.68	0.000
CB*SG	−636	−2.71	0.030
CB*CF	−526	−2.24	0.060
SG*CF	−1379	−5.89	0.001

TABLE XIII
Factorial Design Analysis for Ultimate Tensile Strength (MPa)

Term	Effect	T	P
Constant		127.38	0.000
CB	−21.23	−13.56	0.000
SG	−61.56	−39.32	0.000
CF	1.50	0.96	0.370
CB*SG	6.16	3.93	0.006
CB*CF	6.93	4.42	0.003
SG*CF	−3.33	−2.12	0.071

TABLE XIV
Factorial Design Analysis for Strain at Ultimate Tensile Strength (%)

Term	Effect	*T*	*P*
Constant		62.71	0.000
CB	−1.321	−14.55	0.000
SG	−3.519	−38.76	0.000
CF	−1.798	−19.80	0.000
CB*SG	−0.359	−3.95	0.006
CB*CF	−0.273	−3.00	0.020
SG*CF	−0.030	−0.33	0.751

carbon fillers, the carbon black/synthetic graphite particles, followed by the carbon black/carbon fiber composites, caused a statistically significant decrease (negative effect term) in the composite strain ($P < 0.05$). There was not a statistically significant effect on the composite strain for the synthetic graphite particle/carbon fiber composite ($P > 0.05$). This means that, for example, when carbon black and synthetic graphite particles were combined, then the strain at the composite ultimate tensile strength was lower (negative effect term) than what would be expected from the additive effect of each single filler.[34]

Flexural test results

The effects and the *T* and *P* values for the flexural modulus are given in Table XV, which shows the values for all of the filler combinations. The addition of any of the single fillers had a statistically significant effect on the flexural modulus at the 95% confidence level ($P < 0.05$). The addition of 10 wt % carbon fiber caused the largest increase (largest and positive effect term) in the flexural modulus. This was followed closely by the addition of 40 wt % synthetic graphite particles, which also caused an increase (positive effect term) in the flexural modulus. The addition of 4 wt % carbon black caused the flexural modulus to decrease (negative effect term). None of the two-filler combinations had a statistically significant effect on the composite flexural modulus ($P > 0.05$).

The effects and the *T* and *P* values for the ultimate flexural strength are given in Table XVI, which shows the values for all of the filler combinations. The addition of any of the single fillers had a statistically significant effect on the ultimate flexural strength at the 95% confidence level ($P < 0.05$). The addition of 10 wt % carbon fiber caused the composite ultimate flexural strength to increase (largest and positive effect term). The addition of 40 wt % synthetic graphite particles had the second largest and negative effect (causes decrease) on the ultimate flexural strength. The addition of 4 wt % carbon black also causes the composite ultimate flexural strength to decrease.

TABLE XV
Factorial Design Analysis for Flexural Modulus (MPa)

Term	Effect	*T*	*P*
Constant		111.26	0.000
CB	−1291	−6.48	0.000
SG	3395	17.05	0.000
CF	3739	18.78	0.000
CB*SG	−30	−0.15	0.886
CB*CF	−278	−1.40	0.205
SG*CF	−158	−0.79	0.454

TABLE XVI
Factorial Design Analysis for Ultimate Flexural Strength (MPa)

Term	Effect	*T*	*P*
Constant		204.96	0.000
CB	−6.55	−5.83	0.001
SG	−17.62	−15.69	0.000
CF	33.91	30.21	0.000
CB*SG	6.54	5.83	0.001
CB*CF	0.17	0.15	0.883
SG*CF	−15.02	−13.38	0.000

Two of the two-filler combinations had a statistically significant effect on the composite ultimate flexural strength. The combination of 40 wt % synthetic graphite particles with 10 wt % carbon fiber produced the largest and negative effect (causes decrease) in the composite ultimate flexural strength. The combination of 4 wt % carbon black with 40 wt % synthetic graphite particles caused a statistically significant increase (positive effect term) in the composite ultimate flexural strength. The composite containing carbon black with carbon fiber did not have a statistically significant effect ($P > 0.05$) on the composite ultimate flexural strength.

The statistically significant results for two of the two-way interactions show that there was an effect on the tensile modulus when different fillers were combined. For the 40 wt % synthetic graphite particles with 10 wt % carbon fiber composites, the statistically significant interaction term indicates that the composite ultimate flexural strength was lower (negative effect term) than what would be expected from the additive effect of each single filler.[34] This means that, for example, when 40 wt % synthetic graphite and 10 wt % carbon fiber were combined, then the ultimate flexural strength of the composite decreased more than what would be expected from the individual additive effects of synthetic graphite and carbon fiber. For the 4 wt % carbon black/40 wt % synthetic graphite particle composites, the statistically significant interaction term indicates that the composite ultimate flexural strength was higher (positive effect term) than what would be expected from the additive effect of each single filler.[34] This means that when 4 wt % carbon black and 40 wt % synthetic graphite were combined, then the ultimate flexural strength of the composite increased more than what

would be expected from the individual additive effects of synthetic graphite and carbon black.

CONCLUSIONS

Adding increasing amounts of conductive carbon fillers will increase the composite thermal and electrical conductivity needed for bipolar plates for fuel cells. These fillers also have an effect on the composite tensile and flexural properties, which are also important for bipolar plates. Considering only the composites containing various amounts of single fillers, we found that the addition of carbon black caused all the flexural and tensile properties to decrease. Adding synthetic graphite particles caused the tensile and flexural modulus to increase. They also caused the ultimate tensile strength and ultimate flexural strength to decrease. Adding carbon fibers caused the tensile and flexural modulus and ultimate flexural strength to increase.

The use of factorial design to analyze the tensile and flexural results allows one to rank the effects of single fillers and combinations of different fillers. In many cases, combining two different fillers caused a statistically significant effect. For example, when 40 wt % synthetic graphite particles and 4 wt % carbon black were combined, the composite ultimate tensile and flexural strength increased more than what would be expected from the individual additive effect of each single filler. It is possible that linkages were formed between the carbon black and synthetic graphite particles, which resulted in improved ultimate tensile and flexural strength. To the authors' knowledge, this is the first time in the literature that a synergistic effect of combining different carbon fillers in a Vectra liquid-crystal polymer on the composite tensile and flexural properties has been observed. For all the formulations in this study, the composites exceeded the targets for flexural strength and tensile strength set by PlugPower and the U.S. Department of Energy.

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References

1. United States Department of Energy. Technical Plan-Fuel Cells: Multi-Year Research, Development, and Demonstration Plan, p 3.4-24. http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf (accessed Oct 2006).
2. Clulow, J. G.; Zappitelli, F. E.; Carlstrom, C. M.; Zemsky, J. L.; Busick, D. N.; Wilson, M. S. Fuel Cell Technology: Opportunities and Challenges, Topical Conference Proceedings of the 2002 AIChE Spring National Meeting, New Orleans, LA, March 2002.
3. Taipalus, R.; Harmia, T.; Zhang, M. Q.; Friedrich, K. Compos Sci Technol 2001, 61, 801.
4. Agari, Y.; Uno, T. J. J Appl Polym Sci 1985, 30, 2225.
5. Bigg, D. M. Polym Eng Sci 1977, 17, 842.
6. Bigg, D. M. Adv Polym Technol 1984, 4, 255.
7. Narkis, M.; Lidor, G.; Vaxman, A.; Zuri, L. J Electrost 1999, 47, 201.
8. Nagata, K.; Iwabuki, H.; Nigo, H. Compos Interfaces 1999, 6, 483.
9. Demain, A. Ph.D. Dissertation, Universite Catholique de Louvain, 1994.
10. King, J. A.; Tucker, K. W.; Meyers, J. D.; Weber, E. H.; Clingerman, M. L.; Ambrosius, K. R. Polym Compos 2001, 22, 142.
11. Murthy, M. V. Proc Soc Plast Eng Annu Tech Conf 1994, 3, 1396.
12. Simon, R. M. Polym News 1985, 11, 102.
13. Mapleston, P. Mod Plast 1992, 69, 80.
14. Donnet, J.-B.; Bansal, R. C.; Wang, M.-J. Carbon Black, 2nd ed.; Marcel Dekker: New York, 1993.
15. Huang, J.-C. Adv Polym Technol 2002, 21, 299.
16. Bigg, D. M. Polym Compos 1987, 8, 1.
17. Wilson, M. S.; Busick, D. N. U.S. Pat. 6,248,467 (2001).
18. Loutfy, R. O.; Hecht, M. U.S. Pat. 6,511,766 (2003).
19. Braun, J. C.; Zabriskie, J. E., Jr.; Neutzler, J. K.; Fuchs, M.; Gustafson, R. C. U.S. Pat. 6,180,275 (2001).
20. Mehta, V.; Cooper, J. S. J Power Sources 2003, 114, 32.
21. Thongruang, W.; Spontak, R. J.; Balik, C. M. Polymer 2002, 43, 3717.
22. Ticona Vectra Liquid Crystal Polymer (LCP) Product Information; Ticona: Summit, NJ, 2000.
23. Chiou, J. S.; Paul, D. R. J Polym Sci Part B: Polym Phys 1987, 25, 1699.
24. Akzo Nobel Electrically Conductive Ketjenblack Product Literature; Akzo Nobel: Chicago, IL, 1999.
25. Asbury Carbons Product Information; Asbury Carbons: Asbury, NJ, 2004.
26. Conoco Carbons Products Literature; Conoco: Houston, TX, 1999.
27. Fortafil Carbon Fibers Technical Data Sheet; Toho Tenax America: Rockwood, TN, 1999.
28. King, J. A.; Morrison, F. A.; Keith, J. M.; Miller, M. G.; Smith, R. C.; Cruz, M.; Neuhalfen, A. M.; Barton, R. L. J Appl Polym Sci 2006, 101, 2680.
29. ISO 291:1997: Plastics—Standard Atmospheres for Conditioning and Testing; International Standard Organization: Geneva, Switzerland, 1998.
30. ASTM Standard D 638: Standard Test Methods for Tensile Properties of Plastics; American Society for Testing and Materials: Philadelphia, 1998.
31. ASTM Standard D 790-03: Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials; American Society for Testing and Materials: Philadelphia, 2004.
32. Konell, J. P.; King, J. A.; Miskioglu, I. Polym Compos 2004, 25, 172.
33. Heiser, J. A.; King, J. A.; Konell, J. P.; Miskioglu, I.; Sutter, L. L. J Appl Polym Sci 2004, 91, 2881.
34. Montgomery, D. C. Design and Analysis of Experiments; Wiley: New York, 1997.