Effects of Carbon Fillers on the Rheology of Highly Filled Liquid-Crystal Polymer Based Resins

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ABSTRACT: Adding conductive carbon fillers to insulating resins increases the composite electrical and thermal conductivity. Often, enough of a single type of carbon filler is added to achieve the desired conductivity while still allowing 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 fiber) were added to Vectra A950RX liquid-crystal polymer. The rheological properties of the resulting single-filler composites were measured. In addition, the rheological properties of composites containing combinations of different carbon fillers were studied via a factorial design. In all cases, the viscosity increased with increasing filler volume fraction and followed a shear-thinning power-law model. The factorial design results indicated that each of the single fillers and all the filler combinations caused a statistically significant increase in the composite viscosity when compared at a shear rate of 500 s^{-1} or at a stress of 10^5 Pa. For composites containing synthetic graphite particles and/or carbon fiber, the viscosity variation with the volume fraction of carbon followed a modified Maron–Pierce equation. When compared at a constant volume fraction of carbon, composites containing carbon black showed viscosity enhancement above and beyond that shown by the other composites. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1646–1656, 2008

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

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. 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, and good dimensional stability.

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.[1–14] 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.[15–18] Thermosetting resins cannot be remelted. Adding these conductive fillers typically increases the viscosity of the resin. The viscosity of the resin must be low enough to be processed (extruded, injection-molded, compression-molded, etc.) into a bipolar plate.

In this work, researchers performed compounding runs and then conducted rheological tests on carbon/Vectra A950RX composites. Vectra 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. 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 on the composite viscosity.

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, namely, high dimensional

TABLE I
Properties of Vectra A950RX from Ticona

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
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. 19.

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.[19,20] The properties of this polymer are shown in Table I.[19]

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.[21] The carbon black is in the form of pellets that are 100 μ to 2 mm in size and, upon mixing into a polymer, easily separate into primary aggregates 30–100 nm long.[21] Figure 1 shows a diagram of this carbon black structure.[21]

Table II shows the properties of Thermocarb TC-300 (Asbury Carbons: Asbury, NJ), which is a primary synthetic graphite that was previously sold by Conoco.[22,23] 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 (Rockwood, TN) 243 carbon fiber, sold by Toho Tenax America, Inc., was the third filler used in this study. Fortafil 243 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 strength of a resin. Fortafil 243 is surface-treated and then formed into pellets by

TABLE II
Properties of the Fillers

Filler property	Ketjenblack EC-600 JD carbon black	Thermocarb TC-300 synthetic graphite	Fortafil 243 carbon fiber
Density (g/cm^3)	1.8	2.24	1.74
Brunauer–Emmett–Teller surface area (m^2/g)	1250	1.4	—
Thermal conductivity at 23°C (W/mK)	≈ 2	600 in the *a* crystallographic direction	20 (axial direction)
Electrical resistivity at 23°C (Ω cm)	0.01–0.1	0.020, carbon powder at 150 psi, parallel to the pressing axis	0.00167
Filler shape	See Figure 1	Acicular	Cylindrical with diameter of 7.3 μ
Size	30–100 nm (aggregate)	1.7 = aspect ratio (length/diameter)	Mean length = 3.2 mm (entire range = 2.3–4.1 mm)
Sieve analysis (wt %)			
+300 μ	—	5.79	—
+ 212 μ	—	12.04	—
+180 μ	—	8.25	—
+150 μ	—	12.44	—
+75 μ	—	34.89	—
+44 μ	—	16.17	—
−44 μ	—	10.42	—
Binder content	—	—	2.6 wt % proprietary polymer that adheres pellets together and promotes adhesion with the matrix
Tensile strength (MPa)	—	—	3800
Tensile modulus (GPa)	—	—	227

The data were taken from refs. 21–24.

Figure 1 Structure of Ketjenblack EC-600 JD.

the manufacturer. A proprietary polymer (sizing) is used as a binder for the pellets that also promotes adhesion with the matrix. Table II shows the properties of this carbon fiber.[24]

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 III. In the tables and following text, the abbreviation 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). We note that increasing the filler amount increases the composite melt viscosity. Because of the large increase in the composite melt viscosity, CB is used only at low loading levels.[25] The maximum single-filler contents that could be extruded were 10 wt % for CB, 80 wt % for SG, and 60 wt % for CF.

Table IV 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 5 wt % for Fortafil 243 CF. Because this project focuses on producing highly conductive composites, the loading levels were chosen so that the filler 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 speci-
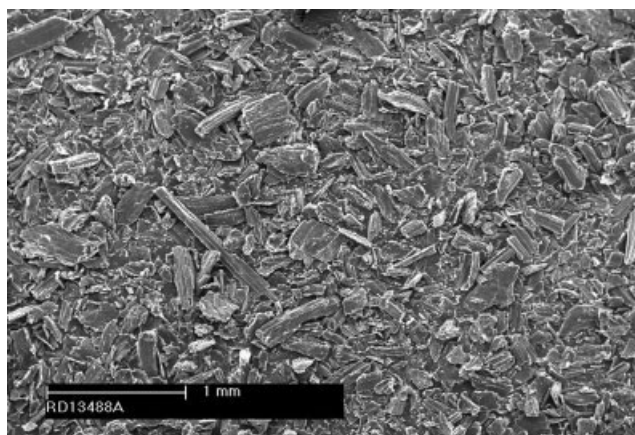

Figure 2 Photomicrograph of Thermocarb TC-300 SG. (Courtesy of Asbury Carbons).

TABLE III
Single-Filler Loading Levels in Vectra A950RX and Power-Law Viscosity Correlation Parameters

Formulation	Filler (wt %)	Filler (vol %)	m (Pa s^n)	n (dimensionless)
Vectra	0.0	0.0	690	0.545 ± 0.007
2.5CB	2.5	1.9	1,300	0.532 ± 0.012
4CB	4.0	3.1	2,700	0.487 ± 0.017
5CB	5.0	3.9	4,700	0.446 ± 0.017
6CB	6.0	4.7	7,500	0.412 ± 0.009
7.5CB	7.5	6.0	18,000	0.346 ± 0.008
10CB	10.0	8.0	50,000	0.287 ± 0.016
10SG	10.0	6.5	590	0.582 ± 0.012
20SG	20.0	13.5	700	0.580 ± 0.017
30SG	30.0	21.1	890	0.577 ± 0.023
40SG	40.0	29.3	2,600	0.495 ± 0.026
50SG	50.0	38.5	6,200	0.450 ± 0.004
60SG	60.0	48.4	22,000	0.362 ± 0.014
65SG	65.0	53.7	22,000	0.388 ± 0.010
70SG	70.0	59.3	55,000	0.313 ± 0.009
75SG	75.0	65.2	57,000	0.379 ± 0.025
80SG	80.0	71.4	78,000	0.387 ± 0.038
10CF	10.0	8.2	750	0.547 ± 0.008
20CF	20.0	16.8	1,300	0.526 ± 0.015
30CF	30.0	25.5	2,500	0.495 ± 0.021
40CF	40.0	34.9	5,700	0.439 ± 0.015
50CF	50.0	44.6	10,000	0.424 ± 0.026
60CF	60.0	54.7	23,000	0.385 ± 0.047

mens. Table V shows the weight percentages and corresponding volume percentages for all of the factorial design formulations (original and replicate). Tables III (including the mean and standard deviation for n) and V also show the power-law viscosity correlation parameters, which are described later in this article.

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. (Sommerville, NJ) model ZSE 27. This extruder has a 27-mm, corotating, intermeshing twin screw with 10 zones and a length/diameter ratio of

TABLE IV
Filler Loading Levels in Factorial Design Formulations

Formulation	Ketjenblack (wt %)	Thermocarb (wt %)	Fortafil (wt %)
No filler	0	0	0
2.5CB	2.5	0	0
65SG	0	65	0
5CF	0	0	5
2.5CB*65SG	2.5	65	0
2.5CB*5CF	2.5	0	5
65SG*5CF	0	65	5
2.5CB*65SG*5CF	2.5	65	5

TABLE V
Filler Loadings in Factorial Design Formulations, Power-Law Viscosity Correlation Parameters, and Viscosity

Formulation	Constituent			m (Pa s^n)	n (dimensionless)	Viscosity (Pa s)	
	Name	wt %	vol %			At 500 s^{-1}	At 10^5 Pa
No filler (Vectra)							
Original	Vectra	100	100	690	0.54	40.7	10.7
Replicate				750	0.53	40.5	9.9
2.5CB							
Original	CB	2.5	1.9	1,300	0.53	70.4	28.1
Replicate	Vectra	97.5	98.1	1,500	0.51	73.8	28.6
65SG							
Original	SG	65	53.7	22,000	0.39	497.1	2095.2
Replicate	Vectra	35	46.3	22,000	0.39	484.3	1958.1
5CF							
Original	CF	5	4.1	570	0.56	37.0	9.8
Replicate	Vectra	95	95.9	560	0.55	34.8	8.5
2.5CB*65SG							
Original	CB	2.5	2.6	210,000	0.25	1963.4	1.768×10^6
Replicate	SG	65	54.1	240,000	0.24	2088.1	3.979×10^6
	Vectra	32.5	43.3				
2.5CB*5CF							
Original	CB	2.5	2.0	2,800	0.48	111.9	59.7
Replicate	CF	5	4.1	3,000	0.48	117.3	65.5
	Vectra	92.5	93.9				
65SG*5CF							
Original	SG	65	54.4	55,000	0.35	945.1	17,917.3
Replicate	CF	5	5.4	56,000	0.34	941.2	18,617.4
	Vectra	30	40.2				
2.5CB*65SG*5CF							
Original	CB	2.5	2.6	540,000	0.18	3059.3	1.275×10^9
	SG	65	54.8				
Replicate	CF	5	5.4	630,000	0.15	3186.6	2.044×10^{10}
	Vectra	27.5	37.2				

40. The screw design, which has been shown elsewhere,[25] was chosen to obtain a minimum amount of filler degradation while still dispersing the fillers well in the polymers. 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, CF was added to the polymer melt at zone 7; CB and SG were 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 nominally 3-mm-long pellets. After compounding, the pelletized composite resin was dried and then stored in moisture-barrier bags before viscosity testing.

Filler length, aspect ratio, and environmental scanning electron microscopy (ESEM) test method

To determine the length and aspect ratio (length/diameter) of the CF and SG in the extruded pellets, di-ethylenetriamine was used to dissolve the matrix. The fillers were then dispersed onto a glass slide and viewed with an Olympus SZH10 optical microscope (Orangeburg, NY) with an Optronics Engineering LX-750 video camera (Goleta, CA). 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 the Image Processing Tool Kit version 3.0. The lengths and aspect ratios of each filler were measured. For each formulation, 1000–6000 particles/fibers were measured. Because of the extremely small size of the CB, the length and aspect ratio of the CB were not measured.

A Phillips XL-40 (Boston, MA) environmental scanning electron microscope was used to view the conductive resin produced in this study.

Capillary rheometer test method

To determine the viscosity, a Goettfert, Inc. (Rock Hill, SC) Rheo-Tester 1000, which is a capillary rheometer, was used. For low shear rates, a 200 bar pressure transducer was used, and a 1400 bar pressure transducer was used for high shear rates. The extruded pellets from all formulations were dried (as described previously in the section on test specimen fabrication) before testing. Four different round-

hole 180° capillaries were used. For the extremely viscous materials, a capillary with a 2-mm diameter that was 20 mm long was used. The other three capillaries had a diameter of 1 mm and lengths of 20, 30, and 40 mm. For each capillary, the same formulation was tested three times at 300°C, which is above Vectra's melting point of 280°C. The viscosities at the following apparent shear rate ($\dot{\gamma}_a$) values were determined: 100, 200, 500, 1000, 2000, and 5000 s^{-1}. For the very viscous materials, the rheometer could not operate at $\dot{\gamma}_a$ values above 500 s^{-1}. $\dot{\gamma}_a$ was calculated as follows:

$$\dot{\gamma}_a = 4Q/\pi R^3 \tag{1}$$

where Q is the volumetric flow rate (mm^3/s) and R is the radius of the capillary (mm).[26] The test method used was ASTM D 3835.[27] Raw data of the pressure drop versus the shear rate were corrected for a nonparabolic velocity profile by use of the Weissenberg–Rabinowitsch correction. The entrance pressure loss (the Bagley correction) was measured to be zero in all cases.[28]

RESULTS

Filler length, aspect ratio, and ESEM results

The length and aspect ratio of the Thermocarb in the composite pellets were typically 50 μ and 1.68, respectively. These values are similar to those of the as-received material and prior work.[29,30] For the composite pellets containing Fortafil 243, the length was typically 70 μ. The corresponding fiber aspect ratio (length/diameter) was 9. These results agree with prior work.[29–31] Figure 3 shows an ESEM photomicrograph at 500× of the conductive resin containing 65 wt % Thermocarb TC-300 SG particles and 5 wt % Fortafil 243 CF in Vectra A950RX. Photomicrographs of CB have been published elsewhere.[12]

Capillary rheometer results

Capillary rheometer tests were conducted on composites containing the following amounts of fillers:

Ketjenblack EC-600 JD CB: 2.5, 4, 5, 6, 7.5, and 10 wt %.
Thermocarb TC-300 SG: 10, 20, 30, 40, 50, 60, 65, 70, 75, and 80 wt %.
Fortafil 243 CF: 5, 10, 20, 30, 40, 50, and 60 wt %.

Polymer rheological data are typically illustrated in a log–log plot of the viscosity as a function of shear rate $\dot{\gamma}$. A horizontal line is indicative of a Newtonian fluid when the viscosity is constant. If the viscosity decreases as the shear rate is increased, the fluid is called shear-thinning. Liquid-crystal polymers usually exhibit shear-thinning behavior.[32–34] They can
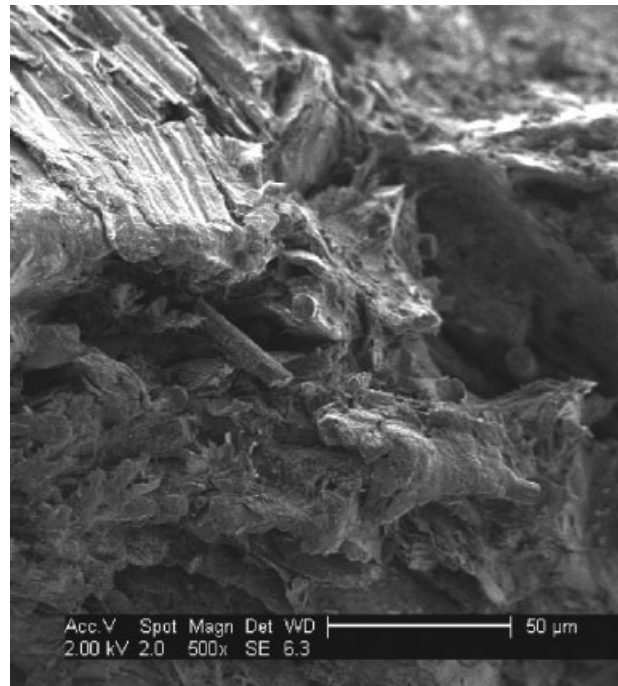
Figure 3 ESEM photomicrograph of the composite containing 65 wt % Thermocarb TC-300 SG particles and 5 wt % Fortafil 243 CF in Vectra A950RX.

also exhibit Newtonian fluid behavior over a narrow range of low shear rates.[32–34] For Vectra A950RX, vendor data suggest shear-thinning behavior.[19]

For capillary fluid flow, the shear stress at the wall [τ_R (Pa)] is given by

$$\tau_R = \frac{R\Delta P}{2L} \tag{2}$$

where ΔP is the pressure drop (Pa) over a capillary of radius R (mm) and length L (mm). For non-Newtonian fluids, the relationship between the true shear rate at the capillary wall ($\dot{\gamma}_R$) and $\dot{\gamma}_a$ (what the shear rate would be for a Newtonian fluid) is given by the following relationship.[26]

$$\dot{\gamma}_R = \dot{\gamma}_a \left[\frac{1}{4} \left(3 + \frac{d \ln \dot{\gamma}_a}{d \ln \tau_R} \right) \right] \tag{3}$$

Equation (3) is valid for any fluid. The quantity in square brackets is called the Weissenberg–Rabinowitsch correction. For Newtonian fluids, the correction factor is 1, and $\dot{\gamma}_R$ is equal to $\dot{\gamma}_a$.

For our experiments, $\dot{\gamma}_a$ was varied (100, 200, 500, 1000, 2000, and 5000 s^{-1}), and the pressure drop was measured with a pressure transducer. On the basis of eq. (2), τ_R was calculated. A quadratic equation was fit to the τ_R–$\dot{\gamma}_a$ data, the derivative in eq. (3) was calculated, and $\dot{\gamma}_R$ was determined. Finally, the steady shear viscosity [η (Pa s)] was calculated with the following equation:[26]
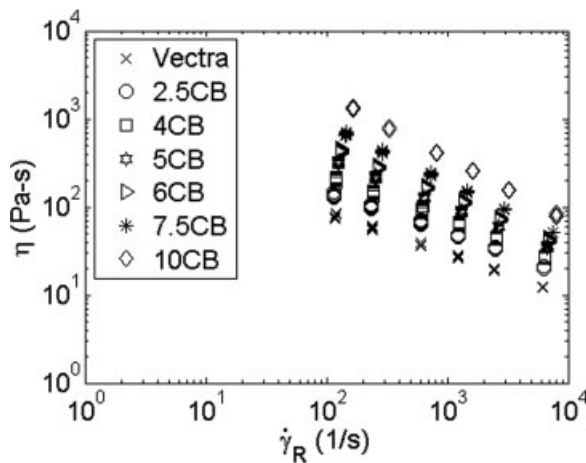
Figure 4 Steady shear viscosity (η) for composites containing Ketjenblack EC-600 JD.

$$\eta = \frac{\tau_R}{\dot{\gamma}_R} \qquad (4)$$

A log–log plot of η (Pa s) as a function of $\dot{\gamma}_R$ (s^{-1}) is plotted in Figure 4 for the composites containing Ketjenblack EC-600 JD CB, in Figure 5 for the composites containing Thermocarb TC-300 SG, and in Figure 6 for the composites containing Fortafil 243 CF. All the data points collected are shown in these figures. Over the range of shear rates studied here, the fluid is shear-thinning. Furthermore, for the data obtained in this study, the η–$\dot{\gamma}_R$ relationship is linear, and thus the composites follow the power-law model:

$$\eta = m\dot{\gamma}_R^{n-1} \qquad (5)$$

where m is the consistency index (Pa s^n) and n (dimensionless) is an exponent that shows the deviation from ideal (Newtonian, $n = 1$) behavior.[26] As
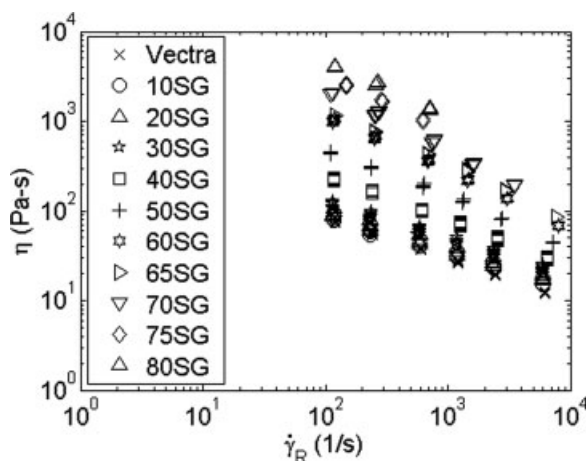

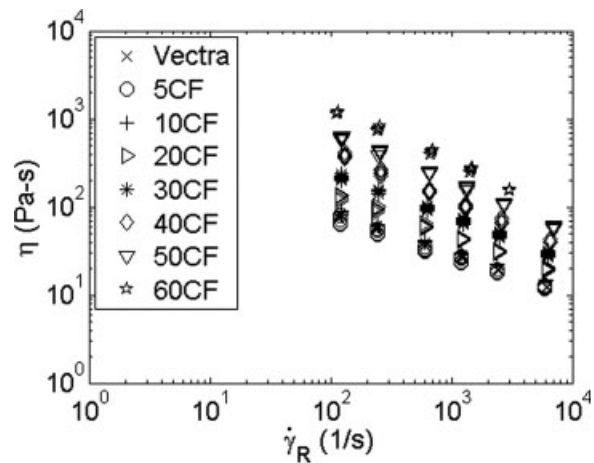**Figure 5** Steady shear viscosity (η) for composites containing Thermocarb TC-300.

Figure 6 Steady shear viscosity (η) for composites containing Fortafil 243.

shown in Figure 5, the composites containing greater than 65 wt % SG could not be run at all the shear rates (the pressures were too high for the capillary rheometer). This is also true in Figure 6 for the composite with 60 wt % CF.

Equation (5) was best fit to each set of rheological data, and the constants m and n are presented in Table III. m increased as the filler loading was increased (from 690 Pa s$^{0.54}$ for pure Vectra A950RX to 50,000 Pa s$^{0.29}$ for highly filled CB composites, 78,000 Pa s$^{0.39}$ for highly filled SG composites, and 23,000 Pa s$^{0.39}$ for highly filled CF composites). The exponent parameter n typically decreased as the filler loading increased (from 0.54 for pure Vectra A950RX down to 0.29 for highly filled CB and 0.39 for the highly filled SG and CF composites).

During testing, no significant die swell or entrance pressure losses were noted for any of the composites. Vectra itself does not show these effects, and the literature reports for other carbon-filled systems indicate that the addition of a filler reduces only die swell and entrance pressure effects.[35,36]

The Maron–Pierce equation for the variation of the relative viscosity (η_r) with the volume fraction of the filler (ϕ) in a concentrated suspension has been found to fit many systems, even shear-thinning systems, provided that the comparison is done at a constant shear stress[35,36]:

$$\eta_r = \frac{\eta(\phi)}{\eta(\phi = 0)} = \frac{1}{\left(1 - \frac{\phi}{A}\right)^2} \qquad (6)$$

The parameter A is related to a maximum allowable volume fraction of filler particles, and a value of $A = 0.637$ represents random close packing of spheres, whereas $A = 0.44$ has been found to correspond to rough, irregular particles. For single-component composites of CB, SG, and CF with Vectra, a plot of

the relative viscosity versus the volume fraction at a shear stress of 10^5 Pa yields the relationships shown in Figure 7. The single-component composites of SG and CF follow a single curve, and for all but the highest ϕ compositions, that curve is bracketed by the Maron–Pierce model for rough, irregular particles and the same model evaluated for random, close-packed spheres. The viscosity-enhancing effects of SG and CF are thus believed to be due to the volume-filling effect of adding particles of different shapes. The two highly filled composites with $\phi > 0.64$ deviate slightly from the general trend; this may be due to wall slip at these high stresses. The CB–Vectra composites are qualitatively different from the SG and CF composites, as previously reported.[25] CB–Vectra blends exhibit an abrupt increase in viscosity at low volume fractions that is not related to the geometric constraints of the filler but is related, we believe, to the unique connective structures that CB is known to form.[12,21,37,38] The CB–Vectra composite data follow a simple exponential model:

$$\eta_r(\text{Vectra} - \text{CB}) = 0.2494 e^{96.952\phi} \tag{7}$$

where ϕ is the volume fraction of carbon in the composite. Below $\phi = 0.64$, the SG- and CF-containing composites lie on a common curve that follows a modified Maron–Pierce equation:

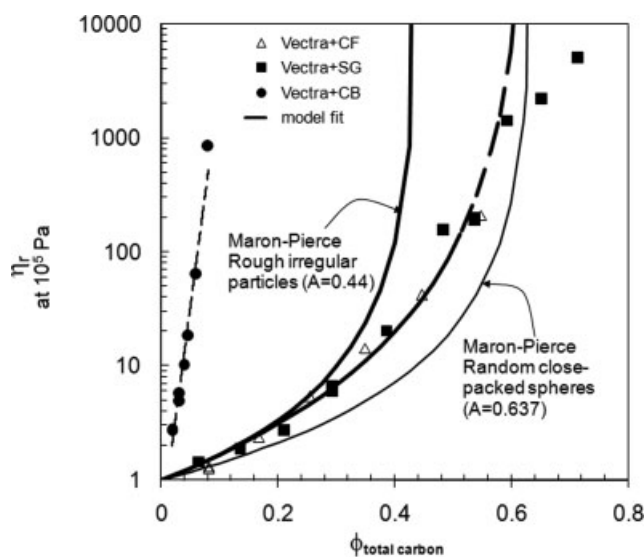$$\eta_r(\text{Vectra} - \text{SG or CF}) = \frac{1}{\left(1 - \frac{\phi}{0.633}\right)^3} \tag{8}$$

Figure 7 Relative viscosity (η_r) at a stress of 100,000 Pa for single-component blends of Vectra with various carbon fillers. Also shown are the predictions of the Maron–Pierce model with A values given; the best fit lines to the data are for the models described in the text.
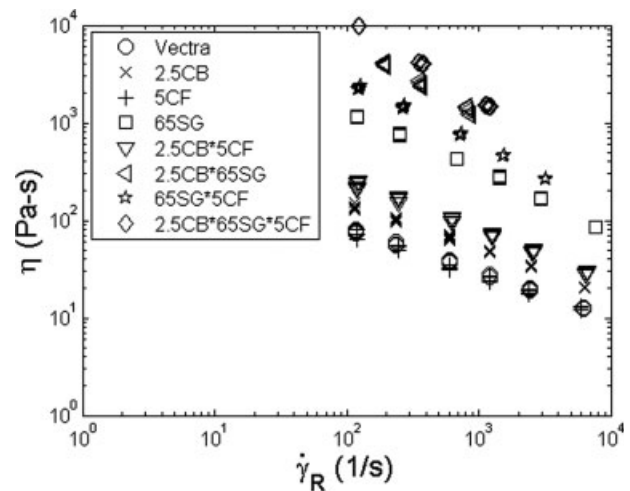
Figure 8 Steady shear viscosity (η) for factorial design composites.

Note that to obtain reduced viscosities at the common stress of 10^5 Pa, it was necessary to extrapolate the power-law viscosity functions for the most viscous data sets (60SG, 65SG, 70SG, 75SG, 80SG, 60CF, and 10CB) to lower values of stress and thus to high values of viscosity.

Figure 8 shows the steady shear viscosity for the factorial design formulations corresponding to that shown in Tables IV and V. Again, for the higher shear rates for the highly filled composites, the viscosity could not be measured. When two-filler blends of the different carbon fillers were tested, the exceptional behavior of CB-containing composites was once again observed (Fig. 9). Figure 9 includes data reported here and previously reported,[39] which
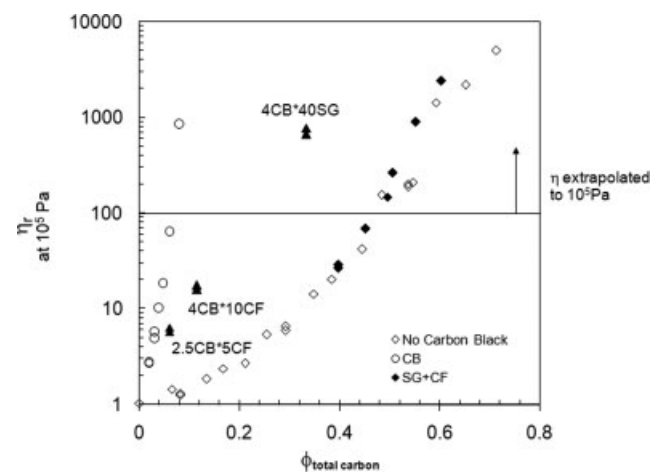
Figure 9 Relative viscosity (η_r) at a stress of 100,000 Pa for single-component (open symbols) and two-filler (closed symbols) blends of Vectra with various carbon fillers. All data above $\eta_r = 100$ are extrapolated.

include combinations of fillers with 4 wt % CB (4CB), 40 wt % SG (40SG), and 10 wt % CF (10CF). Two-filler blends of SG and CF with Vectra follow the same curve of the relative viscosity versus the volume fraction of carbon as was traced by the single-component composites of these materials. Thus, no extraordinary interaction of these two fillers was observed. Two-filler blends containing CB, however, showed significantly enhanced relative viscosity compared to other composites with similar volume fractions of carbon (Fig. 9, composites 2.5CB*5CF, 4CB*10CF, and 4CB*40SG). We believe that the presence of CB in these two-filler systems introduced connectivity among carbon particles of all types, resulting in a significantly enhanced viscosity. This viscosity enhancement is undesirable from the point of view of processing these composites into bipolar plates.

Using viscosities at a common stress of 10^5 Pa for the most highly filled systems, 2.5CB*65SG and 2.5CB*65SG*5CF, would have required an extrapolation to extremely high values of the viscosity. To compare these two blends to the rest of the dataset without these extrapolation issues, we chose to compare them to a reference viscosity at a constant shear rate of 500 s^{-1}. These data are shown in Figure 10. The comparison in Figure 10 confirms the observation that composites with CB are qualitatively and quantitatively different from composites that do not contain CB. When compared at a constant shear rate, the viscosities of CB-containing blends are roughly half a decade higher in viscosity when compared to those of non-CB-containing blends with the same volume fraction of carbon. Note that the augmentation of viscosity is approximately the same for composites with 2.5 wt % CB and 4 wt % CB. It appears that for low-CB-containing composites, the enhancement effect is independent of the amount of CB present. Our prior work[25] shows that the electrical conductivity percolation threshold for CB is 3.7 vol % (4.7 wt %).

The surface texture of the extrudate from the capillary rheometer varied somewhat with the filler volume fraction and with the filler type. The bare Vectra extrudate had a characteristic glossy but mottled surface texture that reflected the crystalline structure of the solid. For the Vectra–SG, Vectra–CF, and Vectra–CB composites, the addition of filler followed the pattern previously reported:[25] for 2.5CB, the composite was dark black and glossy; for 5CF, the extrudate was light gray, and the surface was glossy and had the Vectra surface texture; and for 65SG, the surface was matte and mostly smooth. The two-filler blends varied in appearance, depending on the overall volume fraction of carbon: composite 2.5CB*5CF (ϕ = 0.061) was glossy with the Vectra surface texture, and composites 2.5CB*65SG (ϕ = 0.567) and
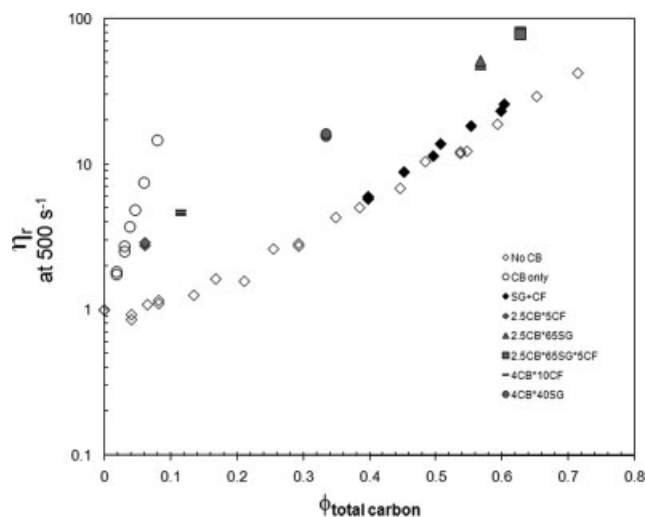

Figure 10 Relative viscosity (η_r) at a shear rate of 500 s^{-1} for single-component (open symbols) and multicomponent (closed symbols) blends of Vectra with various carbon fillers.

65SG*5CF (ϕ = 0.598) were similar in appearance, with a matte texture and a mostly smooth surface. The three-filler composite 2.CB*65SG*5CF (ϕ = 0.628) had a smooth, matte texture at low flow rates and showed surface cracking at high flow rates.

FACTORIAL DESIGN ANALYSIS

Figure 8 is a log–log plot of the viscosity (Pa s) as a function of shear rate $\dot{\gamma}_R$ (s^{-1}) for the factorial design formulations (all of the data points from the original are shown; the replicate data points are not shown, but are very similar to the original data) that correspond to Tables IV and V. Several observations can be made from Figure 8. The viscosities of the 5CF composite and the pure polymer are similar. The following composites are listed in order of increasing viscosity:

$$2.5CB < 2.5CB^*5CF < 65SG < 65SG^*5CF$$
$$< 2.5CB^*65SG < 2.5CB^*65SG^*5CF.$$

Table V shows the m and n values for these factorial design formulations. Following the expected trend, the value for m increases with an increasing amount of filler. The average m values range from 720 Pa s$^{0.535}$ for pure Vectra to 10^5 Pa s$^{0.165}$ for 2.5CB*65SG*5CF. The value for n decreases with increasing filler load as expected on the basis of the single-filler results (Table III). The smallest n value reported is for the 2.5CB*65SG*5CF combination (n = 0.165).

Table V also displays the mean viscosity at $\dot{\gamma}_R = 500$ s^{-1} for the factorial design formulations (original and replicate). With these results, an analysis of the factorial design was conducted with the mean viscosity at $\dot{\gamma}_R = 500$ s^{-1} 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 viscosity were calculated. Small p values indicate that a factor (filler in this case) may have a significant effect on the composite viscosity.[40] 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 viscosity 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.[40]

The effects and P values are given in Table VI, which shows the values for all of the filler combinations. Further investigation of Table VI yields some important information regarding the effects that fillers have on the viscosity. First, for the composites containing only single fillers, SG, followed by CB and then CF, caused a statistically significant increase (positive effect term) in the composite viscosity ($P < 0.05$). Adding 5 wt % CF caused approximately one-fourth of the viscosity increase caused by the addition of 65 wt % SG. All the combinations of different fillers had a statistically significant effect on the viscosity ($P < 0.05$). These effect terms are positive, and this means that the composite viscosity increases when these different fillers are used together. The composite containing 2.5CB*65SG had the largest effect term, followed by 65SG*5CF, then 2.5CB*5CF, and then 2.5CB*65SG*5CF. These results show that, for example, adding CB to SG in these material systems will cause a significant increase in

the composite viscosity, and this could make these materials more difficult to process into bipolar plates. This is likely due to the highly branched, high-surface-area structure of CB (see Fig. 1 and Table II), which forms a network that causes the composite viscosity to increase. This is also supported by conductivity results for these resins, which show that the thermal and electrical conductivity increases when combinations of different carbon fillers are used.[41]

The statistically significant results for all the filler interactions show that there is an effect on the composite viscosity when different fillers are combined. For example, when CB and SG were combined into a composite, the composite viscosity was higher than what would be expected from the additive effect of each single filler.[40]

Table V also displays the mean viscosities at a shear stress of 10^5 Pa for the factorial design formulations (original and replicate). With the logarithm of the viscosity (Pa s) at a shear stress of 10^5 Pa, an analysis of the factorial design was conducted as described previously. The effects and P values are given in Table VII, which shows the values for all of the filler combinations. Further investigation of Table VII yields some important information regarding the effects that the fillers have on the viscosity. First, for the composites containing only single fillers, SG, followed by CB and then CF, caused a statistically significant increase (positive effect term) in the composite viscosity ($P < 0.05$). Adding 5 wt % CF caused approximately one-fourth of the viscosity increase caused by the addition of 65 wt % SG. All the combinations of different fillers had a statistically significant effect on the viscosity ($P < 0.05$). These effect terms are positive, and this means that the composite viscosity increases when these different fillers are used together. The composite containing 2.5CB*65SG had the largest effect term, followed by 65SG*5CF, then 2.5CB*5CF, and then 2.5CB*65SG*5CF. These same trends can be seen in Table VI for the viscosity analysis at a shear rate of 500 s^{-1}.

TABLE VII
Factorial Design Analysis for the Logarithm of the Viscosity (Pa s) at 10^5 Pa

Term	Effect	P
Constant		0.000
2.5CB	2.460	0.000
65SG	4.619	0.000
5CF	1.133	0.000
2.5CB*65SG	1.822	0.000
2.5CB*5CF	0.681	0.003
65SG*5CF	0.987	0.000
2.5CB*65SG*5CF	0.483	0.015

TABLE VI
Factorial Design Analysis for Viscosity (Pa s) at 500 s^{-1}

Term	Effect	P
Constant		0.000
2.5CB	956.2	0.000
65SG	1579.9	0.000
5CF	396.9	0.000
2.5CB*65SG	901.2	0.000
2.5CB*5CF	173.0	0.000
65SG*5CF	377.9	0.000
2.5CB*65SG*5CF	149.4	0.000

CONCLUSIONS

The objective of this research was to determine the effects and interactions of each filler and filler combination on composite rheological properties. For all formulations, the power-law parameter m increased and the power-law parameter n decreased with the addition of filler. The addition of filler to the liquid-crystal polymer matrix always resulted in increased viscosity at a shear rate of 500 s^{-1} or at a stress of 10^5 Pa. A factorial design analysis of formulations containing single-filler materials and combinations of filler materials was performed to determine the significance of each filler and filler combination. Over the range of viscosities studied, all formulations exhibited shear-thinning behavior and follow power-law formulas.

An analysis of the single-filler material formulations shows an increase in the formulation viscosity with an increasing amount of filler. For each filler material (CB, SG, and CF), the viscosity increased with increasing filler content. At a shear rate of 500 s^{-1}, the viscosity of pure Vectra was 40 Pa s. There was a substantial increase in the viscosity at the highest filler loading levels, with 610 Pa s for 10 wt % Ketjenblack CB, 1800 Pa s for 80 wt % Thermocarb SG, and 520 Pa s for 60 wt % Fortafil CF.

Formulations containing single fillers and combinations of fillers were investigated for statistical significance with respect to the formulation viscosity. A 2^3 factorial design was conducted on the basis of the following formulations: Vectra, 2.5CB, 65SG, 5CF, 2.5CB*65SG, 2.5CB*5CF, 65SG*5CF, and 2.5CB*65SG*5CF. It was found that all individual fillers and all combinations of fillers had a statistically significant effect, which increased the composite viscosity at the shear rate of 500 s^{-1}. The significance of the effects followed this order:

$$65SG > 2.5CB > 2.5CB^*65SG > 5CF > 65SG^*5CF$$
$$> 2.5CB^*5CF > 2.5CB^*65SG^*5CF$$

The statistically significant result for all the filler interactions shows that there is an effect on the composite viscosity when different fillers are combined. For example, when CB and SG were combined into a composite, the composite viscosity was higher than what would be expected from the additive effect of each single filler.[40] This result was likely due to the different carbon fillers forming a network, which caused the composite viscosity to increase. To the authors' knowledge, these statistically significant two-filler interactions have never been reported previously in the open literature for this material system.

A comparison of the viscosity behavior shows that addition of SG and CF affects the composite viscosity in a similar manner. The effect caused by these two carbon fillers appears to be due to a filler-packing effect, as reflected in the modified Maron–Pierce equation. All composites that contained CB exhibited enhanced viscosities over and above what would be expected from a purely volumetric effect. It is believed that this difference was due to the well-known tendency for CB to form extended structures. Measurement of the viscosity in the highest ϕ composites may have been affected by wall slip.

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