FEM Calculations of Capillary Rheometer Flow for Carbon-Filled Liquid Crystal Polymer Composites

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ABSTRACT: There is an emerging market for conductive resins for use in fuel cell bipolar plates. This research focuses on developing a finite element model of a capillary rheometer. Comsol Multiphysics 3.2b was used to model the flow of a remeltable thermoplastic matrix material, Vectra A950RX Liquid Crystal Polymer, with varying amounts of either a carbon black or synthetic graphite filler, to obtain the velocity profile and pressure drop of these composites within the capillary. Previous experimental results have shown that the molten composites obey a shear-thinning power law behavior. When comparing the model predicted pressure drops from the model with the experimental data, very good agreement was obtained. This signifies that the rheological behavior of the composites can be described by a power law relationship, using parameters specific to each composite. When comparing the modeled velocity profile with the theoretical profile, it was found for all composite formulations that the velocity becomes fully developed within a length of 0.05 times the diameter of the tube, independent of the power law parameters n and m. This work is a necessary first step in developing 2D or 3D mold filling simulations for fuel cell bipolar plate applications. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 433–438, 2007

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

INTRODUCTION

Most polymer resins are thermally and electrically insulating. Increasing both types of conductivity of these resins allows them to be useful in more applications than would be otherwise possible. One emerging market for conductive resins is bipolar plates for use in fuel cells. The plates separate one cell from the next, with hydrogen gas on one side and air (to supply 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 thermal and/or electrical conductivity of a polymer is through the addition of a conductive filler material, such as carbon or a 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] Once a thermosetting resin has solidified it cannot be melted and reformed, which is a significant disadvantage. Consequently, this research focused on using a remeltable thermoplastic resin for the matrix material.

In prior work[19] we reported on the rheological properties of carbon-filled Vectra A950RX. Vectra is a thermoplastic that can be remelted and used again. A carbon black and a synthetic graphite were studied as filler materials as a function of filler content. Viscosity parameters were tested, using capillary rheometry, and the composites were found to follow the power-law model for shear viscosity based on standard interpretations of capillary rheometry data. The power-law generalized Newtonian constitutive equation predicts much more than the relationships exploited in capillary rheometry, however.[20] When used to simulate 2D or 3D flows such as in molding simulations, the other assumptions of the Power Law Generalized Newtonian Fluid (PL-GNF) will come into play, such as the failure to predict shear normal stresses and the failure to predict elasticity or memory. It is therefore somewhat unwise to infer full power-law constitutive behavior from curve fits to viscosity-shear rate curves alone.

As a partial test to the constitutive behavior of the Vectra composites studied here, finite-element modeling was performed on a flow domain that matches the geometry of the capillary rheometer barrel and capillary. This flow includes the entire up-stream barrel flow and the entry-flow region, in which there is both shear and elongation. The calculated pressure

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profiles were compared with measured entry and exit pressure values. Also calculated was the distance down the capillary required for the flow to become fully developed. This entry effect was compared with the measured Bagley corrections for the composites. Although full 3D flow profiles were not measured nor simulated, the comparisons described here are one additional step that can be taken to verify the power-law constitutive behavior of materials before engaging in 2D, 3D, or other complex simulations.

MATERIALS AND EXPERIMENTAL METHODS

Materials

The matrix used for this project was Ticona's Vectra A950RX Liquid Crystal Polymer (LCP) (Summit, NJ), which is a highly ordered thermoplastic copolymer consisting of 73 mol % hydroxybenzoic acid and 27 mol % hydroxynaphtholic acid. This LCP has the properties needed for bipolar plates, namely high dimensional stability up to a temperature of 250°C, extremely short molding times (often 5–10 s), exceptional dimensional reproducibility, chemical resistance in acidic environments of fuel cells, and a low hydrogen gas permeation rate.[21,22] The properties of this polymer are shown in Table I.

The first filler used in this study was Ketjenblack EC-600 JD. This is an electrically conductive carbon black available from Akzo Nobel (Chicago, IL). The highly branched, high surface area carbon black structure allows it to contact a large amount of polymer, which 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. The carbon black is sold in the form of pellets that range from 100 μm to 2 mm in size and upon mixing into a polymer, easily separates into primary aggregates 30–100 nm long.[23] Figure 1 shows a diagram of the carbon black structure.

TABLE I
Properties of Ticona's Vectra A950RX[21]

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^2
Density at 23°C	1.40 g/cc
Volumetric electrical resistivity at 23°C	10^{15} ohm cm
Surface electrical resistivity	10^{14} ohm
Thermal conductivity at 23°C	0.2 W/mK (approx.)
Humidity absorption (23°C/50% RH)	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

TABLE II
Properties of Akzo Nobel Ketjenblack EC-600 JD[23]

Electrical resistivity	0.01–0.1 Ohm cm
Aggregate size	30–100 nm
Specific gravity	1.8 g/cm^3
Apparent bulk density	100–120 kg/m^3
Ash content (max.)	0.1 wt %
Moisture (max.)	0.5 wt %
BET surface area	1250 m^2/g
Pore volume	480–510 cm^3/100g

Table III shows the properties of the Asbury Carbons' Thermocarb TC-300 (Asbury, NJ), which is a synthetic graphite that was previously sold by Conoco (Houston, TX).[24,25] 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.[24]

The viscosity of composites containing varying amounts of these carbon fillers in Vectra A950RX were measured.[19] The concentrations (shown in wt % and the corresponding vol %) for these single filler composites are shown in Tables IV and V. Note that these tables also display additional parameters that will be defined later in this article. Prior work with nylon 6,6 and polycarbonate has shown that the concentrations selected for these fillers will yield thermally and electrically conductive resins.[26–28] Typically, for bipolar plate applications, 60–70 wt % synthetic graphite is used.[15]

Test specimen fabrication

For this project the fillers were used as they were 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 (Somerville, NJ), Model ZSE 27. This extruder has a 27-mm corotating intermeshing twin screw with 10 zones and a length/diameter ratio of 40. The screw design is shown elsewhere.[19] It was chosen to allow a large concentration of 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

Figure 1 Structure of Ketjenblack EC-600 JD.

TABLE III
Properties of Thermocarb TC-300 Synthetic Graphite[24,25]

Filler	Thermocarb TC-300 synthetic graphite
Carbon content (wt %)	99.91
Ash (wt %)	<0.1
Sulfur (wt %)	0.004
Density (g/cc)	2.24
BET Surface Area (m^2/g)	1.4
Thermal Conductivity at 23°C (W/mK)	600 in ''a'' crystallographic direction
Electrical resistivity of bulk carbon powder at 150 psi, 23°C, parallel to pressing axis (ohm-cm)	0.020
Particle shape	Acicular
Particle aspect ratio	1.7
Sieve analysis, Microns (wt %)	
+600 microns	0.19
+500 microns	0.36
+300 microns	5.24
+212 microns	12.04
+180 microns	8.25
+150 microns	12.44
+75 microns	34.89
+44 microns	16.17
−44 microns	10.42

fillers into the polymer melt. Two 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 followed by a pelletizer that produced nominally 3 mm long pellets. After compounding, the pelletized composite resin was dried again and stored in moisture barrier bags prior to rheology testing.

Capillary rheometer test method

To determine viscosity, a Goettfert, Rheo-Tester 1000 (Rock Hill, SC), which is a capillary rheometer was used. For low shear rates a 200 bar pressure transducer was used, and for high shear rates a 1400 bar pressure transducer was used. The extruded pellets from all formulations were dried (as described previously) prior to testing. Three different round-hole, 180° capillaries were used. Each capillary had a diameter of 1 mm. The lengths of the three capillaries were 20, 30, and 40 mm. For each capillary, the same formulation was tested three times at 300°C, a temperature above Vectra's melting point of 280°C. The viscosities at the following apparent shear rates, $\dot{\gamma}_a$, were determined: 100, 200, 500, 1000, 2000, and 5000 s^{-1}. The apparent shear rate, $\dot{\gamma}_a$, was calculated using eq. (1) shown below:

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

where Q is the volumetric flow rate (in units of mm^3/s), and R is the radius (in units of mm) of the capillary.[20] The test method used was ASTM D3835.[29] Raw data of pressure drop versus shear rate were corrected for nonparabolic velocity profile by use of the Weissenberg–Rabinowitsch correction. Entrance pressure loss, i.e., the Bagley Correction was measured to be zero in all cases.[30]

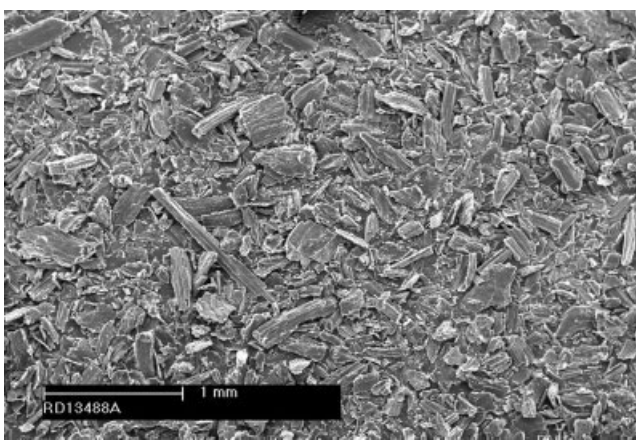

Figure 2 Photomicrograph of Thermocarb TC-300 Synthetic Graphite.[24]

TABLE IV
Single Filler Loading Levels of Ketjenblack EC-600 JD in Vectra A950RX and Power Law Viscosity Correlation Parameters

Filler (wt %)	Filler (vol. %)	m (Pa-s^n)	n (dimensionless)
0.0	0.0	690	0.54
2.5	1.9	1300	0.53
4.0	3.1	2700	0.49
5.0	3.9	4700	0.45
6.0	4.7	7500	0.41
7.5	6.0	18,000	0.35
10.0	8.0	50,000	0.29

Finite element modeling

Previous research[19] has shown that the capillary shear rheometry of Vectra/carbon black and Vectra/synthetic graphite systems can be described as a power law fluid. A model was developed for the flow of a power law fluid within the capillary rheometer, using Comsol Multiphysics version 3.2b (Burlington, MA).

TABLE V
Single Filler Loading Levels of Thermocarb TC-300 in Vectra A950RX and Power Law Viscosity Correlation Parameters

Filler (wt %)	Filler (vol. %)	m (Pa-s^n)	n (dimensionless)
0.0	0.0	690	0.54
10.0	6.5	611	0.58
20.0	13.5	700	0.58
30.0	21.1	890	0.58
40.0	29.3	2300	0.51
50.0	38.5	6200	0.45
60.0	48.4	22,000	0.36
70.0	59.3	80,000	0.29

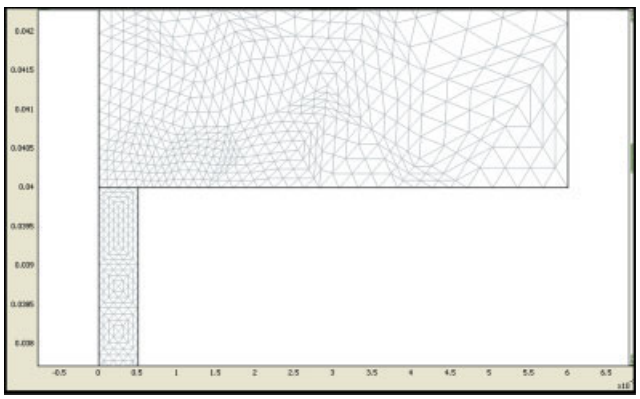

Figure 3 Axisymmetric finite element mesh (near capillary entrance) as produced by Comsol Multiphysics 3.2b. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The capillary rheometer consists of two cylinders, the larger upstream barrel, and the much smaller downstream capillary. The upper cylinder is the reservoir and measures 6 mm in radius and 225 mm in length. The lower cylinder is the capillary and measures 0.5 mm in radius. The length of the capillary is varied to be 20, 30, or 40 mm, with the number of elements in the simulation as 4432, 5392, and 6352, respectively.

In our simulations, an axisymmetric 2D model was developed. No-slip boundary conditions were used on the outer surfaces, with symmetry at the centerline. The entrance velocity profile was constant and the outlet pressure was set to be zero. A partial mesh of the capillary rheometer geometry is shown in Figure 3.

RESULTS

As stated earlier, the capillary shear viscosity of Vectra/carbon black and Vectra/synthetic graphite systems can be described as a power law fluid,[19] where the viscosity η is a function of the shear rate $\dot{\gamma}$ according to:

$$\eta = m\,\dot{\gamma}^{n-1} \tag{2}$$

where m is the consistency index (in units of Pa-s^n) and n (dimensionless) is an exponent, which shows the deviation from ideal (Newtonian) behavior.[20] It is noted that the consistency index m increased as the filler loading was increased, and the exponent parameter n typically decreased as the filler loading increased. The m and n parameters for the composite resins tested here are shown in Tables IV and V.

Capillary rheometer modeling results

Velocity profile results

The velocity behavior of the polymer in a capillary with a length-to-diameter ratio of 20 was modeled, using Comsol Multiphysics 3.2b. From the models, velocity data were obtained radially across the capillary over its entire length. These data were then compared with the theoretical velocity profile. The results were consistent for each of the samples in determining at which position within the capillary tube the polymer reaches its fully-developed velocity profile (that matching the theoretical velocity), providing useful information about the necessary length-to-diameter ratio for measuring the pressure drop across the capillary.

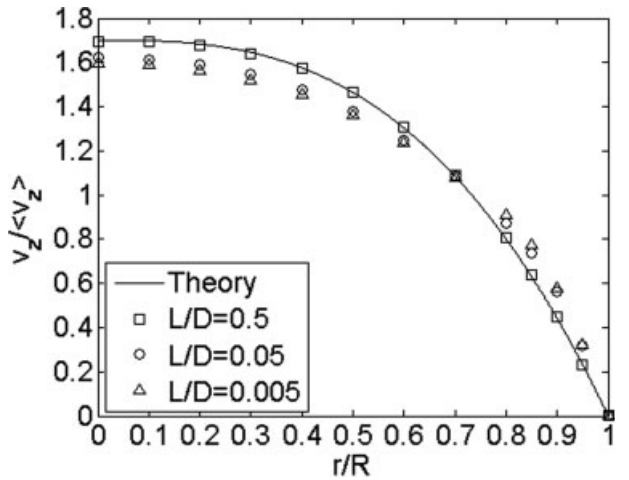

Figure 4 Capillary velocity profile for pure Vectra at L/D values of 0.5, 0.05, and 0.005 downstream of the capillary entrance.

Separate simulations were run for pure Vectra, composites containing 6 and 10 wt % Ketjenblack, and composites containing 30 and 70 wt % Thermocarb, by varying the power law parameters m and n. The theoretical velocity profile v_z as a function of the distance r from the center of the capillary was found for each system using eq. (3) for a power-law fluid:

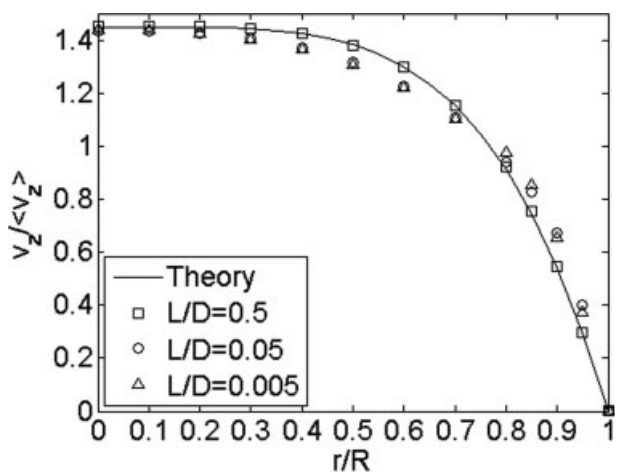

Figure 5 Capillary velocity profile for 10 wt % carbon black in Vectra at L/D values of 0.5, 0.05, and 0.005 downstream of the capillary entrance.

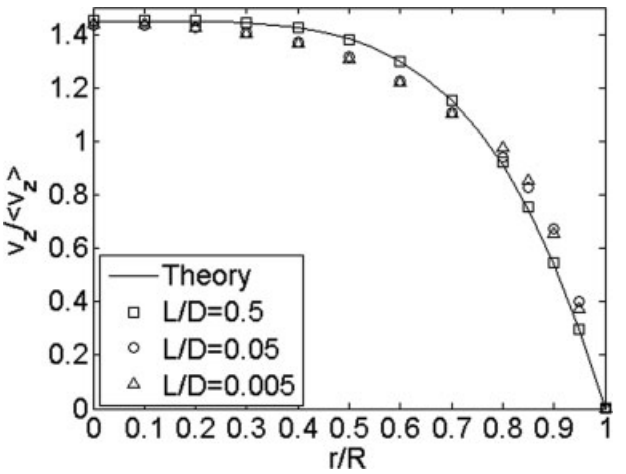

Figure 6 Capillary velocity profile for 70 wt % Thermocarb in Vectra at L/D values of 0.5, 0.05, and 0.005 downstream of the capillary entrance.

$$\frac{v_z}{\langle v_z \rangle} = \frac{1+3n}{1+n}\left(1 - \left(\frac{r}{R}\right)^{n+1/n}\right) \tag{3}$$

where R is the radius of the capillary and $\langle v_z \rangle$ is the cross-sectional average velocity.

By plotting the reduced velocity as given by eq. (3) at different lengths along the capillary axis, one can discern the length of capillary necessary for the velocity profile to become fully developed. These plots are given in Figures 4–6 for pure Vectra, a Vectra polymer composite containing 10 wt % carbon black, and a Vectra polymer composite containing 70 wt % Thermocarb, respectively. The results are at a shear rate of 100 s^{-1} and are consistent for each substance modeled and show that the velocity profile becomes fully developed at a distance of 0.05 diameters downstream of the capillary entrance. Since the experiments were run using capillary length-to-diameter ratios of 20, 30, and 40, measurements of pressure drops across these lengths will be valid.

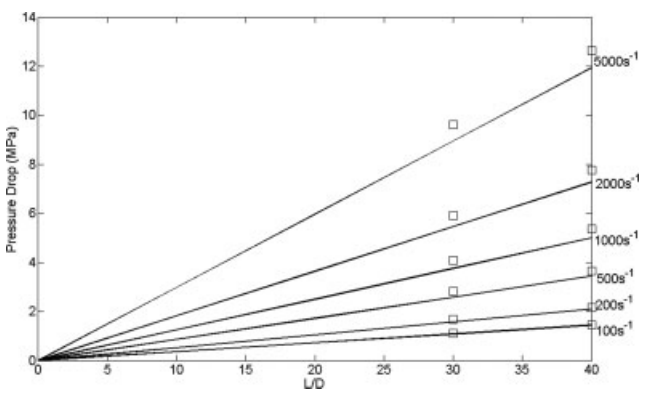

Figure 7 Bagley plot comparing simulation (lines) and experiment (squares) for pure Vectra.

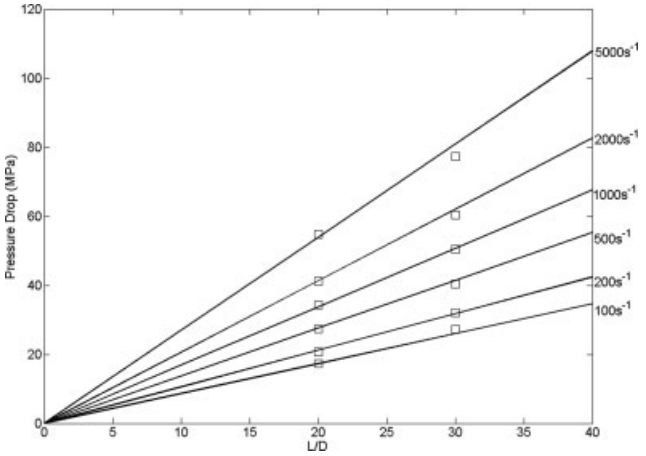

Figure 8 Bagley plot comparing simulation (lines) and experiment (squares) for Vectra composites containing 10 wt % carbon black.

Pressure drop results

As mentioned earlier, the experimental pressure drop across the capillary rheometer was measured, using a pressure transducer placed in the barrel near the top of the capillary, and the pressure at the exit of the capillary is atmospheric. The Comsol Multiphysics 3.2b models used in the previous subsection were used to predict the pressure drop across the capillary. First, at both the entrance and exit of the capillary, the pressure distributions across the face of the surface were calculated, using the Comsol software. From these distributions, the cross-sectional average pressure was obtained at the entrance and exit of the capillary. The difference between these values is the model-predicted pressure drop. This calculation was performed for each composite formulation, at each shear rate, and for the experimental L/D values of 20, 30, and 40.

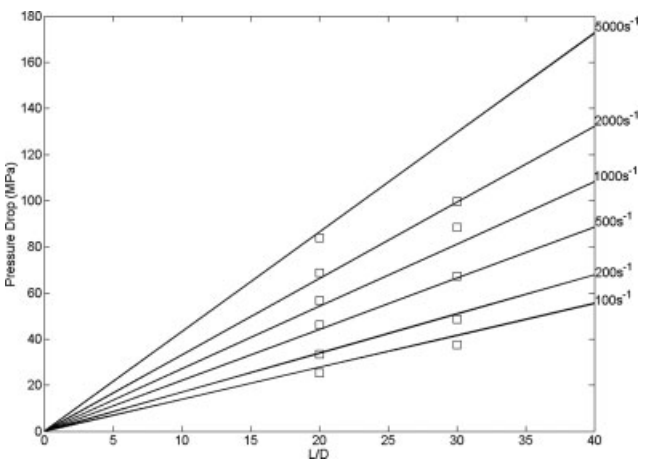

Figure 9 Bagley plot comparing simulation (lines) and experiment (squares) for Vectra composites containing 70 wt % Thermocarb.

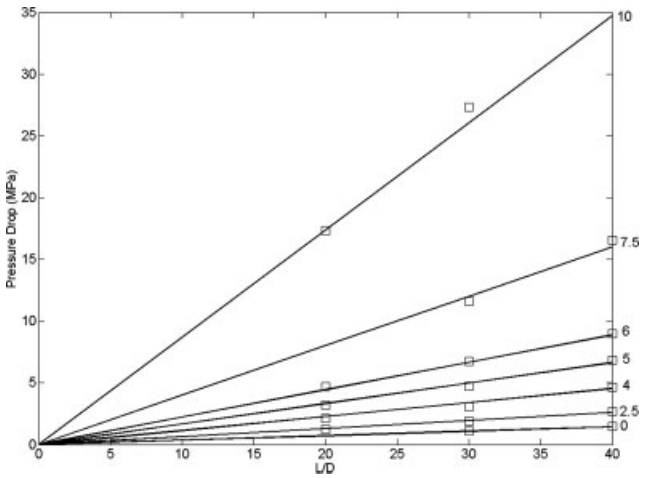

Figure 10 Bagley plot for all carbon black filled systems at a shear rate of 100 s^{-1}.

Plots of the FEM results (lines) and the experimental data (squares) are shown for the various shear rates for pure Vectra, Vectra composites containing 10 wt % carbon black, and Vectra composites containing 70 wt % Thermocarb in Figures 7–9. These plots are commonly referred to as Bagley plots.[20,30] It is noted that for each formulation studied, the multiple lines correspond to the various shear rates. The FEM results pass through the origin, signifying no significant loss of pressure at the inlet to the capillary due to rearrangement of the velocity profile and the presence of elongational flow. This is the expected result for the PL-GNF constitutive model. The experimental data match up well with the model prediction (the pressure transducer is accurate within $\pm$10%). As a final comparison, Figure 10 shows the pressure drops over the capillary for all of the carbon black-filled systems at a constant apparent shear rate of 100 s^{-1}. A similar plot can also be made for the Thermocarb systems.

CONCLUSIONS

This project focused on the capillary shear behavior of a remeltable thermoplastic resin, Vectra A950 RX, filled with varying quantities of either a carbon black, Ketjenblack EC600-JD, or a synthetic graphite, Thermocarb TC-300. The goal was to investigate more completely the accuracy of using the power-law generalized Newtonian constitutive model for these systems. Predictions using the PL-GNF were made by using the finite-element method with Comsol Multiphysics 3.2 to model the flow in the barrel and in the capillary. By comparing the theoretical power-law velocity profile to the FEM results, it was found that the velocity profile fully develops to match the theoretical power law velocity within a distance of 0.05 times the diameter of the tube-a distance much less than the length of any of the tubes used-independent of the filler quantity. Experimental measurements of the pressure drops over the length of the tubes were found to be consistent with the FEM-calculated values using the PL-GNF model. The pressure-drop calculations support the use of an inelastic model such as the PL-GNF for modeling these composite systems.

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