Evaluation of Electrical Conductivity Models for Conductive Polymer Composites

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ABSTRACT: The electrical conductivity of polymeric materials can be increased by the addition of carbon fillers, such as carbon fibers and graphite. The resulting composites could be used in applications such as interference shielding and electrostatic dissipation. Electrical conductivity models are often proposed to predict the conductivity behavior of these materials in order to achieve more efficient material design that could reduce costly experimental work. The electrical conductivity of carbon-filled polymers was studied by adding four single fillers to nylon 6,6 and polycarbonate in increasing concentrations. The fillers used in this project include chopped and milled forms of polyacrylonitrile (PAN) carbon fiber, Thermocarb™ Specialty Graphite, and Ni-coated PAN carbon fiber. Material was extruded and injection-molded into test specimens, and then the electrical conductivity was measured. Data analysis included a comparison of the results to existing conductivity models. The results show that the model proposed by Mamunya, which takes into account the filler aspect ratio and the surface energy of the filler and polymer, most closely matched the conductivity data. This information will then be used in the development of improved conductivity models. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1341–1356, 2002

Key words: electrical conductivity; percolation theory; conductive composites; carbon composites; plastics; modeling; conducting polymers

INTRODUCTION

The electrical conductivity of polymeric materials can be increased by the addition of carbon fillers, such as carbon fibers, carbon black, and graphite.[1–3] The resulting composites can be used in applications where metals have typically been the materials of choice.[4–7] The possible applications include electromagnetic and radio-frequency in-terference (EMI/RFI) shielding for electronic devices and electrostatic dissipation (ESD). Electrical conductivity models are often proposed to explain and predict the conductivity behavior of these composites. Development of more accurate models would allow for more efficient materials design and could therefore reduce costly experimental work as well as reduce material and production costs through optimized design.

To study the electrical conductivity of carbon-filled polymers, four different carbon fillers were added to nylon 6,6 and polycarbonate in increasing concentrations. The fillers used in this project include two forms (3.175-mm chopped and 200-μm milled) of polyacrylonitrile (PAN)-based

carbon fibers, Thermocarb™ Specialty Graphite, and Ni-coated PAN carbon fiber. Only single fillers were added to each polymer, and there were no combinations of fillers studied. A total of 42 formulations were produced and studied with the goal of developing equations to describe the electrical conductivity of composite systems.

BACKGROUND

The electrical conductivity of a composite is generally characterized by its dependence on the filler volume fraction. At low filler loadings, the conductivity of the composite is still very close to that of the pure polymer matrix. At some critical loading, called the percolation threshold, the conductivity increases several orders of magnitude with very little increase in the filler amount. After this region of drastic increase, the conductivity once again levels off and is close to that of the filler material. This is at the percolation threshold where enough filler has been added so that it begins to form a continuous conductive network through the composite.

Various models have been proposed in an effort to predict the electrical conductivity behavior of composites based on numerous factors. While all the models base calculations on the filler volume fraction, there are other factors that can affect the conductivity of the composite, as well as the volume fraction at which the percolation threshold occurs. Physical properties of both the filler and the polymer will influence the composite and include structural properties, interfacial properties, and constituent conductivity.

Typical conductivity values for polymers range from 10^{-14} to 10^{-17} Siemens/cm (S/cm). In contrast, the electrical conductivity of carbon fillers can range from 10^2 to 10^4 S/cm, compared to metals, which are typically around 10^6 S/cm. The different forms of carbon, such as fibers or carbon black, usually have different inherent conductivity, and it is this value that typically controls the upper bound of the conductivity curve. In the region of a higher filler amount, the composite's conductivity should level off to a value equal to or slightly lower than that of the filler. Ultimately, the value at which the conductivity levels off at is often dependent on other properties of the composite as well.

The properties of the filler that play a significant role in determining the conductivity of the composite include filler type, size, and shape. Different forms of carbon generally have different structure and properties and, therefore, will affect the electrical conductivity in different ways. The shape of the filler particle has been shown to alter the conductivity. For spherical particles, a smaller particle size will lower the percolation threshold,[8] while for particles with an aspect ratio (ratio of length to diameter, *L/D*) greater than 1, larger aspect ratios and a broader range of aspect ratios will lower the percolation threshold.[9–11]

The surface properties of the filler and polymer also have a significant effect on the conductivity of the composite[5] by influencing the interaction between them. How well the polymer wets the surface of the filler can be quantified by the difference between the surface energies of the two materials.[12] Smaller differences between the two surface energy values lead to better wetting of the filler by the polymer. Better wetting means that larger amounts of the polymer are coating the filler surface, which will alter the distribution of the filler within the matrix. This will increase the percolation threshold and the overall resistivity of the composite because larger amounts of filler are required before the particles will come in contact with each other. It is for this reason that a somewhat larger difference between the surface energy of the filler and the polymer is desirable.

Due to the distinct influence these parameters have on a composite system, four main classes of conductivity models have been developed and can be found in the literature. They include statistical, thermodynamic, geometrical, and structure-oriented models, as described in detail by Lux.[13] Each class predicts the electrical conductivity based on distinct approaches to accounting for the parameters described above.

Statistical Percolation Models

Most of the models found in the literature are of the statistical percolation type. These models typically predict the conductivity based on the probability of particle contacts within the composite. Two of the early percolation models often referenced were originally proposed by Kirkpatrick[14] and Zallen.[15] A finite regular array of points, such as face-centered cubic or body-centered cubic, and bonds between points were used to determine the percolation concentration. By computer simulation, it was possible to predict the points and bonds that were in a cluster and to determine if that cluster spanned the boundaries of the sys-

tem. It was then possible to predict the percolation threshold, but further calculations were required to convert the predicted values into volume fractions. The model that was proposed followed a power-law equation of the following form:

$$\sigma = \sigma_0(V - V_c)^s \quad (1)$$

where σ is the conductivity of the mixture; σ_0, the conductivity of the filler; V, the volume fraction of the filler; V_c, the volume percolation fraction; and the critical exponent s, dependent upon the dimension of the lattice.

This particular model was not completely accurate in calculating the electrical conductivity. However, it has become the basis for many of the later conductivity models. As a result, they have become slightly more accurate predictors of electrical conductivity.

Bueche[16] tried to explain the problem of conductive particles in an insulating matrix based on the concept of polymer gelation. The resulting equation is given by

$$\rho = \frac{\rho_m\rho_f}{(1 - V_f)\rho_f + V_f\omega_g\rho_m} \quad (2)$$

where ρ is the resistivity of the mixture; ρ_m, the resistivity of the insulator; ρ_f, the resistivity of the conductor; V_f, the volume fraction of the conductive phase; and ω_g, the weight fraction of the conductive phase in an infinite cluster, a function of the number of contacts per particle and the probability of contact.

Since polymer gelation is considered a classical statistical percolation problem, there are parallels between the original percolation problem discussed by Zallen. Bueche's equation was able to account for the different drastic jumps in conductivity, only if the correct value for the maximum number of contacts per particle was chosen, on which the model was highly dependent. However, the calculated values from this model did not match the experimental data.

Another example of an improved statistical model was proposed by McLachlan.[17] In his article, McLachlan suggested that this particular model could be used for any system comprising a high conductivity material embedded in a poorly conducting material, an example of which is the system studied here. This model is based on a general effective media equation and is similar in

form to a statistical model. The equation of interest is similar in form to a statistical model, which takes into account the conductivities of constituent materials and is given by

$$\frac{(1 - \phi)(\rho_m^{1/t} - \rho_h^{1/t})}{\rho_m^{1/t} + \left(\dfrac{1 - \phi_c}{\phi_c}\right)\rho_h^{1/t}} + \frac{\phi(\rho_m^{1/t} - \rho_l^{1/t})}{\rho_m^{1/t} + \left(\dfrac{1 - \phi_c}{\phi_c}\right)\rho_l^{1/t}} = 0 \quad (3)$$

where ρ_m is the resistivity of the composite; ρ_h, the resistivity of the component with high resistivity; ρ_l, the resistivity of the component with low resistivity; ϕ, the volume fraction; ϕ_c, the percolation threshold; and t, the critical exponent.

In this model, the critical exponent, t, can be determined either by a calculation or by curve-fitting techniques. McLachlan showed in his article that the exponent is a function of the demagnetization or depolarization coefficients of the low- and high-resistivity materials. However, if this information is not known, then the exponent could be determined by curve fitting.

Thermodynamic Models

Mamunya et al.[12,18] studied the composite conductivity versus the filler volume fraction for different polymers in a way that allowed them to evaluate the influence of other factors on the conductivity. These factors included filler and polymer surface energies and polymer melt viscosity, among others. By taking these particular factors into account, this model fits into the thermodynamic model category. The resulting model showed that the percolation behavior was dependent on the polymer–filler interaction, in addition to the size and amount of the filler material. At all points above the percolation threshold, the conductivity of the composite was found to be

$$\log \sigma = \log \sigma_c + (\log \sigma_m - \log \sigma_C)\left(\frac{\phi - \phi_c}{F - \phi_c}\right)^k \quad (4)$$

and

$$k = \frac{K\phi_c}{(\phi - \phi_c)^{0.75}} \quad K = A - B\gamma_{\mathrm{pf}}$$

where σ is the composite conductivity; σ_c, the conductivity at the percolation threshold; σ_m, the conductivity at F; F, the maximum packing fraction; ϕ, the volume fraction; AR, the aspect ratio;

ϕ_c, the percolation threshold; γ_{pf}, the interfacial tension; and A and B, constants.

The value k is dependent upon the filler volume fraction, percolation threshold, and interfacial tension as calculated by the Fowkes[19] equation:

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

where γ_{pf} is the interfacial tension; γ_p, the surface energy of the polymer; and γ_f, the surface energy of the filler. This model produced good agreement between the calculated values and the experimental data for a number of different polymers filled with carbon black[12]; however, it was not extended to include other types of fillers. To apply this model to the study here, an equation from an earlier study by this same group was used to calculate F, the maximum packing fraction, for carbon fibers.[18] This equation is given by

$$F = \frac{5}{\dfrac{75}{10 + AR} + AR} \qquad (6)$$

It will be shown that the addition of this equation into the model allows for the accurate calculation of electrical conductivity for composites containing carbon fibers.

Geometrical Percolation Models

According to Lux,[13] this class of percolation models was originally intended to predict the conductivity of sintered mixtures of conducting and insulating powders. The major assumption is that during the sintering process the insulating material forms regular cubic particles, while the conductive particles arrange in a regular manner on the surface of the insulating particles. The main parameters used in determining the conductivity are the diameters of the nonsintered particles or the edge length of the sintered particles.

A well-known model in this class is the one proposed by Malliaris and Turner.[20] There are two equations used to predict two volume fractions—one to calculate the percolation threshold, and the other, for the volume fraction at the end of the conductivity increase. These equations use the diameter of the particles, the probability for the occurrence of long bands of conductive particles, and the arrangement of the conductive particles on the surface of the insulating particles.

Through the author's experimental comparison, it was determined that their equations were not able to accurately predict the volume fractions.

Structure-oriented Models

Structure-oriented models are based on the physical construction of the final composite. The electrical conductivity of composite materials is often affected by structural properties such as the filler aspect ratio and filler orientation. These properties are typically a result of the processing techniques employed to make the composite. For example, injection molding a composite will cause an alignment of fillers within a polymer due the flow through the nozzle and the mold. Alignment of the fillers can result in different conductivity results depending on the direction of measurement. Extrusion and injection-molding processes can also degrade fillers, shortening the lengths.

One structure-oriented model was proposed by Nielsen,[2] which related the conductivity of a composite to the aspect ratio (L/D) and the coordination number of the filler. The equations used in Nielson's model are as follows:

$$\sigma_c = \sigma_{poly}\frac{1 + AB\phi_f}{1 - B\Psi\phi_f} \qquad (7)$$

$$B = \frac{\sigma_f/\sigma_{poly} - 1}{\sigma_f/\sigma_{poly} + A} \quad \Psi \approx 1 + \left(\frac{1 - \phi_m}{\phi_m^2}\right)\phi_f$$

where ϕ_f is the volume fraction of filler; σ_c, the composite conductivity; σ_{poly}, the polymer conductivity; σ_f, the filler conductivity; and ϕ_m, the maximum packing fraction.

In this model, A is a function of the aspect ratio and B is essentially equal to 1 for polymer systems. Nielsen used these equations to describe the electrical conductivity, the thermal conductivity, and the modulus of metal/polymer systems. While the equation is marginally accurate for thermal conductivity estimates, Bigg[7] showed that it is completely ineffective in predicting the electrical conductivity.

Weber and Kamal[21] proposed two models accounting for the filler concentration, dimensions, aspect ratio, and orientation. The system studied was nickel-coated graphite fibers in polypropylene. The "end-to-end" model assumed that the sample consisted of conductive "strings" of fibers and that they are connected end-to-end. Another model was proposed which took into account the

Table I   Properties of Nylon 6,6 (Zytel 101 NC010)[22]

Melting Point	262°C
T_g (glass transition temperature, DAM)	60–70°C (approx.)
50% relative humidity	23°C (approx.)
Melt flow rate	12.35 g/10 min
Shear viscosity at 1000 s^{-1} shear rate and 280°C	137 Pa s
Tensile strength at 23°C (DAM)	82.7 MPa
Flexural modulus at 23°C (DAM)	2827 MPa
Tensile elongation at break at 23°C (DAM)	60%
Notched Izod impact, 23°C	53 J/m
Density at 23°C	1.14 g/cm^3
Electrical resistivity at 23°C	10^{15} ohm cm
Thermal conductivity at 23°C	0.25 W m^{-1} K^{1}

fiber–fiber contacts in addition to the other parameters. The resulting equation for the contact is given by

$$\rho_{c,\text{long}} = \frac{\pi d^2 \rho_f X}{4\phi_p d_c l \cos^2\theta} \qquad (8)$$

$$X = \frac{1}{0.59 + 0.15m} \quad \phi_p = \beta\phi \quad \beta = \frac{\phi - \phi_{\text{crit}}}{\phi_t - \phi_{\text{crit}}}$$

where $\rho_{c,\text{long}}$ is the longitudinal composite conductivity; ρ_f, the filler resistivity; X, the function of the number of contacts; d/dc, the ratio of the diameter of the fiber to the diameter of the circle of contact; l/d, the aspect ratio; ϕ_p, the percentage of fibers participating in strings; θ, the angle of orientation; ϕ_t, the "threshold" value at which all fibers participate in strings; and ϕ_{crit}, the percolation threshold.

While some structure-oriented models can accurately predict conductivity, a major limitation to all models in this class is that they do not account for or can predict the surface-energy interactions that have been shown to have a signif-

icant effect on the conductivity of the composite. The thermodynamic model by Mamunya et al.[12] showed that the conductivity is intimately related to the surface interactions of the polymer and the filler.

EXPERIMENTAL

Materials

For this study, two different polymers were used as matrix materials. These were DuPont (Wilmington, DE) Zytel 101 NC010, an unmodified, semicrystalline nylon 6,6, and GE Plastics (Pittsfield, MA) Lexan HF1110-111N (polycarbonate), an amorphous engineering thermoplastic. The electrical conductivities of Zytel and Lexan are approximately 10^{-15} and 10^{-17} S/cm, respectively. The properties of nylon 6,6 (ref. 22) and polycarbonate[23] can be found in Tables I and II. Akzo Nobel (Rockwood, TN) Fortafil carbon fibers were used for two of the carbon fillers.[24] A 3.175-mm chopped and pelletized PAN-based carbon fiber, sized for polycarbonate (Fortafil 201)

Table II   Properties of Polycarbonate (Lexan HF1110-111N)[23]

Melt index	25 g/10 min
Average molecular weight	Approximately 16,000 g/gmol
Tensile strength at 23°C	65.474 MPa
Flexural modulus at 23°C	2309.87 MPa
Tensile elongation at break at 23°C	120%
Density at 23°C	1.20 g/cc
Notched Izod impact, 23°C	640 J/m
Volumetric electrical resistivity at 23°C	10^{17} ohm cm
Thermal conductivity at 23°C (ASTM C177)	0.19 W m^{-1} K^{-1}

Table III   Properties of Chopped PAN-Based Carbon Fibers[24]

Sized For	Polycarbonate (Fortafil 201)	Nylon 6,6 (Fortafil 243)
Carbon content	95%	95%
Tensile strength	3790.6 MPa	3790.6 MPa
Tensile modulus	2.27×10^5 MPa	2.27×10^5 MPa
Electrical resistivity	0.00167 ohm cm	0.00167 ohm cm
Thermal conductivity	20 W m^{-1} K^{-1} (axial direction)	20 W m^{-1} K^{-1} (axial direction)
Density	1.72 g/cm^3	1.74 g/cm^3
Fiber diameter	7.3 microns	7 microns
Filament shape	Round	Round
Bulk density	0.371 g/cm^3	0.356 g/cm^3
Mean length	0.125 in. (0.9–0.16 in.)	0.125 in. (0.9–0.16 in.)

and nylon 6,6 (Fortafil 243), was used. The second form of carbon fibers was a milled and pelletized PAN-based carbon fiber, with an average length of 200 μm, sized for nylon 6,6 (Fortafil 482) and polycarbonate (Fortafil 402). The properties for the chopped PAN fibers can be found in Table III, with the properties of the milled fibers found in Table IV. The third filler was Thermocarb™ Specialty Graphite, available from Conoco, Inc (Ponca City, OK).[25] The properties of this high-purity synthetic graphite can be found in Table V. The final filler used for this project was a 6.35-cm chopped and pelletized Ni-coated PAN-based carbon fiber obtained from Composite Materials, LLC. (Mamaroneck, NY), the properties of which are listed in Table VI.

Materials were assigned a letter and were cataloged according to the assigned letters and the target weight percent. For example, the composite made from 10 wt % PAN carbon fiber in nylon 6,6 would be given the name of "AN10." The formulations made are listed in Table VII.

Methods

Test Specimen Preparation

For this project, the polymers were first dried in a dehumidifying drier. The nylon 6,6 and the polycarbonate were dried at 79 and 121°C, respectively. All fillers were used as received and were not dried. Materials were extruded using a 27-mm corotating intermeshing twin-screw extruder with an *L/D* ratio of 40 (American Leistritz Extruder Corp. ZES27) and 10 zones. The screw design was chosen to obtain the maximum possible electrical conductivity by minimizing the filler degradation. Polymer pellets were put into the extruder in zone one, with a side stuffer located in zone seven to introduce the carbon fillers. After the extrusion process, the formulations were pelletized and dried according to the previously described conditions prior to injection molding. Test specimens were formed using an injection molder (Niigata, NE85UA$_4$) with a 40-mm-diameter single screw having an *L/D* ratio of 18. The test parts

Table IV   Properties of Milled PAN-based Carbon Fibers[24]

Sized For	Polycarbonate (Fortafil 402)	Nylon 6,6 (Fortafil 482)
Carbon content	95%	95%
Tensile strength	3790.6 MPa	3790.6 MPa
Tensile modulus	2.27×10^5 MPa	2.27×10^5 MPa
Electrical resistivity	0.00167 ohm cm	0.00167 ohm cm
Thermal conductivity	20 W m^{-1} K^{-1} (axial direction)	20 W m^{-1} K^{-1} (axial direction)
Density	1.74 g/cm^3	1.74 g/cm^3
Fiber diameter	7.3 microns	7 microns
Filament shape	Round	Round
Bulk density	0.403 g/cm^3	0.413 g/cm^3
Mean length	200 μm (150–250)	200 μm (150–250)

Table V Properties of Thermocarb™ Specialty Graphite[25]

Ash	< 0.1 wt %
Sulfur	0.02 wt %
Vibrated bulk density	0.66 g/cm^3
Density	2.24 g/cm^3
Thermal conductivity at 23C	500 W m^{-1} K^{-1} on a 6 mm particle
Electrical resistivity	10^{-5} ohm cm (approximate)
Particle aspect ratio	2
Particle shape	Irregular

Particle Sizing, Vol % (by Sieve Method)	
+48 Tyler Mesh[a]	4
−48/+80 Tyler Mesh	22
−80/+200 Tyler Mesh	48
−200/+325 Tyler Mesh	16
−325 Tyler Mesh	10

48 Tyler Mesh = 297 microns; 80 Tyler Mesh = 177 microns; 200 Tyler Mesh = 74 microns; 325 Tyler Mesh = 44 microns.

that were molded include 16.51-cm-long tensile bars and 6.35-cm-diameter disks, both 3.175 mm thick.

Longitudinal Electrical Resistivity Test

The first electrical resistivity test was to measure volumetric longitudinal, or in-plane, resistivity. Test specimens cut from the center gauge portion of a tensile bar were surface-ground and then cut into sticks 2 mm wide × 2 mm thick × 25.4 mm long. For each formulation, a total of six specimens were cut from a single tensile bar, and three bars were used to obtain a total of 18 test specimens. These samples were then tested using a

four-probe technique. This technique measures resistivity by applying a constant current (typically 5–10 mA) and measuring the voltage drop over the center 6 mm of the sample. The equation below is then used to calculate the electrical resistivity. A Keithley 224 programmable current source and a Keithley 182 digital sensitive voltmeter were used. Conductivity is calculated by taking the inverse of the electrical resistivity and is given in units of S/cm:

$$ER = \frac{\Delta V w t}{iL} \qquad (9)$$

where ER is the electrical resistivity (in ohm cm); Δ_v, the voltage drop over the center 6 mm of the sample (volts); w, the width (cm); t, the thickness (cm); l, the length (cm); and i, the current (amps).

Transverse Electrical Resistivity Test

For samples of high resistivity ($>10^5$ ohm cm), the transverse, or through-plane, volumetric resistivity test was also run. In this method, a constant voltage, typically 10 or 100 V, was applied to the test specimen and the resistivity was measured according to ASTM D257 (ref. 26) using a Keithley 6517A electrometer/high resistance meter and an 8009 resistivity test fixture. For each formulation, five specimens were tested. Each were disks of 6.35 cm in diameter and 3.175 mm thick. For both resistivity methods, all nylon 6,6-based samples were tested dry-as-molded and the polycarbonate samples were conditioned at 50% relative humidity and 23°C and then tested.

Optical Microscopy Analysis

To determine the aspect ratio of the fillers, microscopy techniques were applied. Approximately

Table VI Properties of Ni-coated PAN-based Carbon Fibers

Sized For	Polycarbonate	Nylon
Tensile strength (PAN fiber core)	4479.8 MPa	4479.8 MPa
Tensile modulus (PAN fiber core)	22.75 × 10^5 MPa	22.75 × 10^5 MPa
Elongation (PAN fiber core)	1.90%	1.90%
Electrical resistivity	4.1 × 10^{-5} ohm cm	4.1 × 10^{-5} ohm cm
Thermal conductivity	10.7 W m^{-1} K^{-1}	10.7 W m^{-1} K^{-1}
Density	2.85 g/cm^3	2.85 g/cm^3
Fiber diameter	7.3 μm	7.3 μm
Filament shape	Round	Round
Wt % binder pickup	22.7	10.7
Wt % nickel	45	45

Table VII   Formulation List

Formulation	Zytel 101 NC010 (Nylon 6,6) Matrix N	Nominal Wt % Filler
AN10	3.175-mm chopped PAN carbon fiber (A)	10
AN20	3.175-mm chopped PAN carbon fiber (A)	20
AN30	3.175-mm chopped PAN carbon fiber (A)	30
AN40	3.175-mm chopped PAN carbon fiber (A)	40
AN50	3.175-mm chopped PAN carbon fiber (A)	50
BN10	200-μm milled PAN carbon fiber (B)	10
BN20	200-μm milled PAN carbon fiber (B)	20
BN30	200-μm milled PAN carbon fiber (B)	30
BN40	200-μm milled PAN carbon fiber (B)	40
BN50	200-μm milled PAN carbon fiber (B)	50
FN25	Thermocarb™ Specialty Graphite (F)	25
FN30	Thermocarb™ Specialty Graphite (F)	30
FN35	Thermocarb™ Specialty Graphite (F)	35
FN40	Thermocarb™ Specialty Graphite (F)	40
FN45	Thermocarb™ Specialty Graphite (F)	45
FN50	Thermocarb™ Specialty Graphite (F)	50
GN5	Ni-coated PAN carbon fiber (G)	5.8
GN10	Ni-coated PAN carbon fiber (G)	11.6
GN15	Ni-coated PAN carbon fiber (G)	17.4
GN20	Ni-coated PAN carbon fiber (G)	23.1
GN30	Ni-coated PAN carbon fiber (G)	34.7

Formulation	Lexan HF1110-111N (Polycarbonate) Matrix P	Nominal Wt % Filler
AP10	3.175-mm chopped PAN carbon fiber (A)	10
AP20	3.175-mm chopped PAN carbon fiber (A)	20
AP30	3.175-mm chopped PAN carbon fiber (A)	30
AP40	3.175-mm chopped PAN carbon fiber (A)	40
AP50	3.175-mm chopped PAN carbon fiber (A)	50
BP10	200-μm milled PAN carbon fiber (B)	10
BP20	200-μm milled PAN carbon fiber (B)	20
BP30	200-μm milled PAN carbon fiber (B)	30
BP40	200-μm milled PAN carbon fiber (B)	40
BP50	200-μm milled PAN carbon fiber (B)	50
FP25	Thermocarb™ Specialty Graphite (F)	25
FP30	Thermocarb™ Specialty Graphite (F)	30
FP35	Thermocarb™ Specialty Graphite (F)	35
FP40	Thermocarb™ Specialty Graphite (F)	40
FP45	Thermocarb™ Specialty Graphite (F)	45
FP50	Thermocarb™ Specialty Graphite (F)	50
GP5	Ni-coated PAN carbon fiber (G)	5
GP10	Ni-coated PAN carbon fiber (G)	10
GP15	Ni-coated PAN carbon fiber (G)	15
GP20	Ni-coated PAN carbon fiber (G)	20
GP30	Ni-coated PAN carbon fiber (G)	30

1 g from a composite specimen was placed in an atmospheric oven to remove the polymer from the fillers. A number of different times and temperatures were tested, and it was determined that 1 h and 427°C were the optimum conditions under which to run this test. In addition, carbon fibers were placed into the furnace to determine if there was any weight loss from the process on the fibers, such as charring. The optimum time and temperature did not affect the fibers in any way.

Table VIII   Aspect Ratios of Various Formulations

Sample	Total Counts	Average Length (mm)	Fiber Diameter (mm)	Aspect Ratio
AN	428	0.082	0.006	13.678
BN	446	0.067	0.007	9.546
GN	406	0.179	0.0075	23.821
AP	445	0.117	0.006	19.442
BP	426	0.075	0.007	10.751
GP	447	0.131	0.0075	17.412

From this test, the actual weight percent of the formulation could be determined. The remaining fillers were then dispersed onto a microscope slide and viewed with a light microscope. Computer software was used to determine the lengths of 400–500 individual fibers, and the average, mean, and median values for the lengths were calculated. From this, the aspect ratio could then be calculated, with the results given in Table VIII.

Modeling Analysis

As a part of the analysis of the experimental data, conductivity models taken from the literature survey were examined and applied to this study. Models were chosen based on the parameters that were included in the calculations, mainly surface energy and structure properties. A simple parametric study was first performed to judge the effects of various parameters within a specific model. Once this was complete, the experimental data were examined by comparison to calculated values. Combined with statistical analysis, the ability of the models to accurately predict the conductivity was determined, and several constants within the various models were updated to reflect the results obtained in this study.

RESULTS

The conductivity results for the composites containing chopped PAN-based carbon fibers can be found in Figure 1 for both nylon 6,6 and polycarbonate composites. In each figure, all the data points have been plotted. Figure 2 shows the conductivity values obtained for the milled PAN-based carbon fibers in nylon 6,6 and in polycarbonate. One noticeable difference in each figure is that the conductivity of the nylon 6,6 composites is consistently one to two orders of magnitude greater than that of the corresponding polycarbonate-based composites. At 30 wt % (21.8 vol % actual) of chopped carbon fiber in nylon 6,6, the conductivity is 7.70 S/cm, while the conductivity at 30 wt % (19.73 vol % actual) of chopped carbon
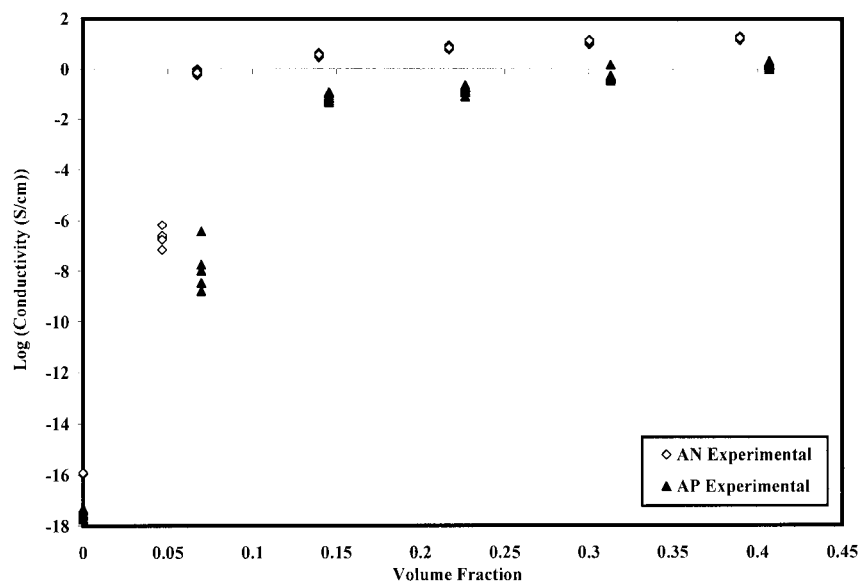

Figure 1   Electrical conductivity results for nylon 6,6 (AN) and polycarbonate (AP) composites containing chopped carbon fibers.
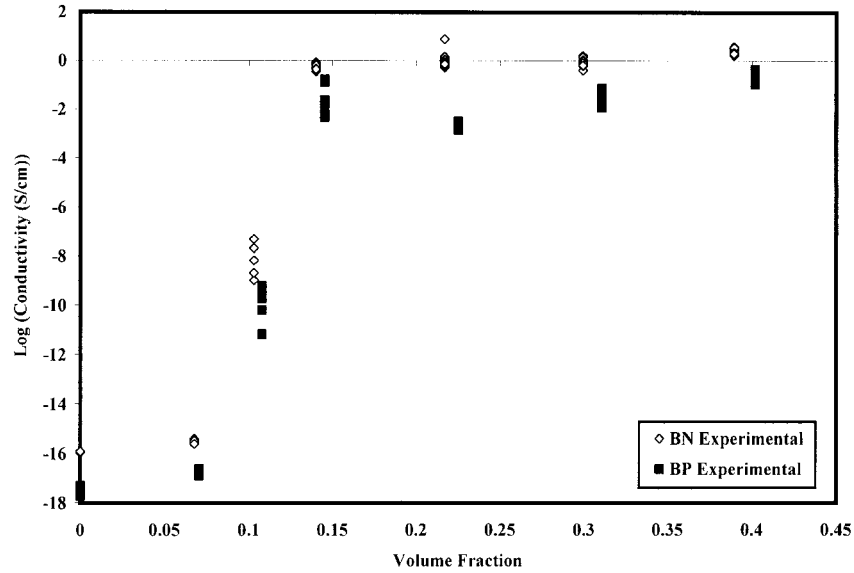
Figure 2 Electrical conductivity results for nylon 6,6 (BN) and polycarbonate (BP) composites containing milled carbon fibers.

fiber in polycarbonate is 0.145 S/cm. These figures illustrate the effects that the polymer matrix has on the composite conductivity. The properties that will influence the conductivity values include polymer conductivity, the degree of crystallinity, and physical properties such as the surface energy. In this case, nylon 6,6 has a higher degree of crystallinity, higher conductivity, and higher surface energy, all of which could lead to the higher conductivity values obtained here.

It is also of significant interest to compare the results of the same polymer with the fillers of differing aspect ratios. This is illustrated in Figure 3, showing the nylon 6,6 composites containing the chopped carbon fiber and milled carbon fiber. The aspect ratio data can be found in Table
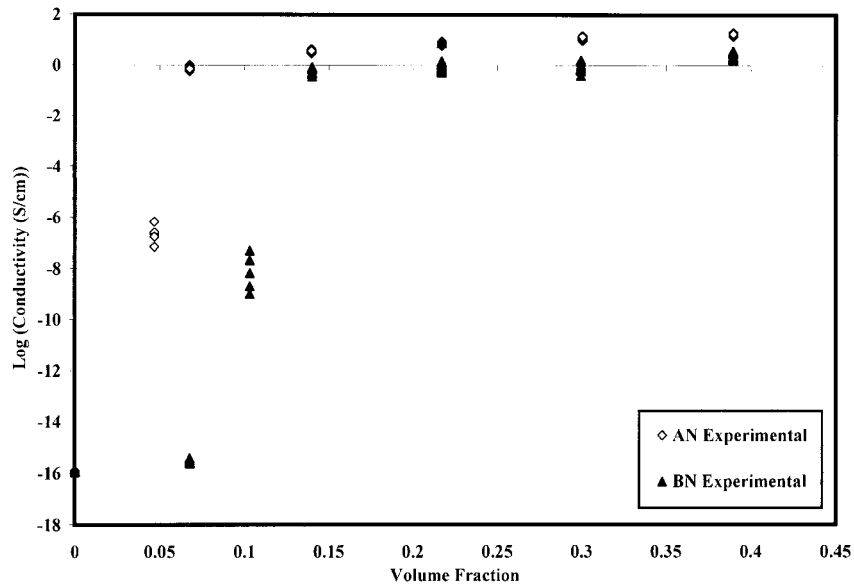
Figure 3 Electrical conductivity results for nylon 6,6 composites containing chopped (AN) and milled (BN) carbon fibers.
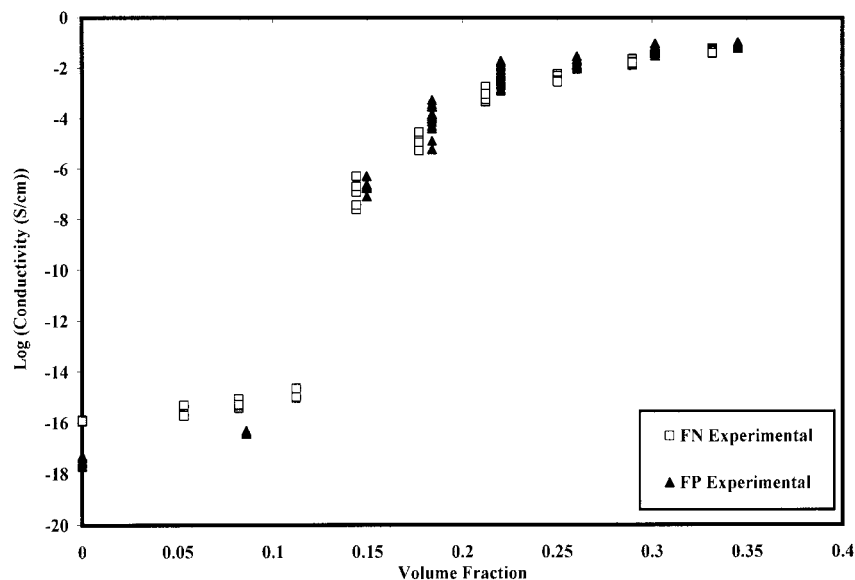
Figure 4 Electrical conductivity results for nylon 6,6 (FN) and polycarbonate (FP) composites containing Thermocarb^{TM} Specialty Graphite.

VIII. The figure shows that the different aspect ratios also have an effect on the conductivity of the composite. The chopped carbon fiber in nylon had an aspect ratio of approximately 14 after processing, while the milled carbon fiber had an aspect ratio of approximately 9.5. This results in the chopped carbon fiber composite having a conductivity at 30 wt % (21.8 vol % actual) filler of 7.70 S/cm and the milled carbon fiber composites having a conductivity of 0.86 S/cm at 30 wt % (21.6 vol % actual). The increased aspect ratio of the chopped fibers of the final composite over the milled fibers produced an increase of conductivity values of approximately one order of magnitude. It also follows that the percolation threshold for the BN composite is slightly higher than that of the AN composite due to the smaller aspect ratio, also illustrated in Figure 3. Similar results were found when comparing the AP to BP formulations. The aspect ratios are different due to both a smaller original size (200-μm milled versus 3.175-mm chopped) and the fact that, although every attempt was made to minimize the effect, there was some degradation of the fibers during the extrusion and injection-molding processes.

Figure 4 shows the results for the electrical conductivity data for the graphite-filled polymers. It can be seen from this figure that Thermocarb^{TM} Specialty Graphite improves the conductivity of the pure polymer. It has a conductivity of approximately 10^5 S/cm, which is about one order of magnitude higher than that of the PAN carbon fibers. However, these formulations do not attain the same conductivity levels reached with composites containing the PAN-based carbon fibers. The conductivity of the nylon 6,6 composite containing Thermocarb^{TM} Specialty Graphite is 1.48 $\times$ 10^{-5} S/cm at 30 wt % (17.06 vol % actual), while the conductivity of the nylon 6,6 composites containing the chopped PAN carbon fibers is 7.70 S/cm at 30 wt % (21.8 vol % actual). One possible reason for this is the aspect ratio effect, similar to what was seen in the previous two carbon fiber composites. The average aspect ratio of the graphite in the injection-molded specimen is approximately two, and it was previously shown that smaller aspect ratios would lead to a decrease in the composite conductivity.

The electrical conductivity data for the composites containing the Ni-coated PAN carbon fibers are found in Figure 5. This figure shows that the percolation threshold for these materials is only slightly lower than that of the other materials. The composites containing the Ni-coated fibers achieve a slightly higher conductivity level. This is largely due to the presence of the nickel metal, which is approximately 10^6 S/cm, as the results for uncoated PAN fibers do not reach high conductivity levels at such low volume fractions. In addition, as shown in Table VIII, the aspect ratio of the Ni-coated PAN-based carbon fibers after processing is higher than that of any other filler.
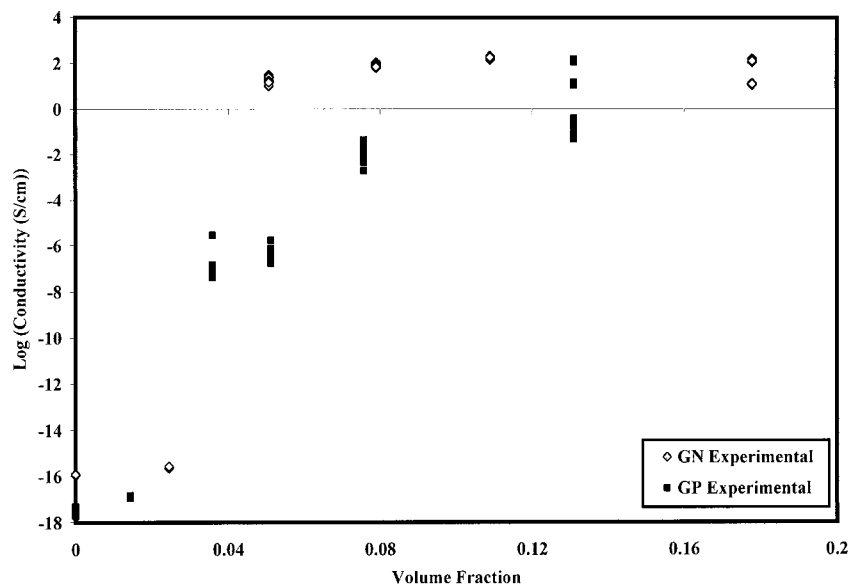
Figure 5 Electrical conductivity results for nylon 6,6 (GN) and polycarbonate (GP) composites containing Ni-coated PAN-based carbon fibers.

CONDUCTIVITY MODELING ANALYSIS

Once the experimental portion of this project was completed, the results were compared to and evaluated according to some of the models described previously. A number of these models, while not specifically generated using carbon–polymer systems, were proposed to explain the conductivity behavior of a wide range of conductive composites. This study was done to test the applicability of these models to the carbon–polymer systems studied here and is the first step in the development of improved electrical conductivity models.

The first model studied was the statistical model by proposed by McLachlan[17] given in eq. (3). In this equation, t is the critical exponent that needs to be estimated. The exponent was determined by matching the calculated values to one set of experimental data to obtain a value for t. The data for the composite of chopped carbon fiber in nylon 6,6 (AN), consisting of the conductivities of the fiber and polymer and the percolation threshold value, were used to obtain a value of t = 2.5. This value for the critical exponent was then used with the electrical resistivity results for chopped carbon fiber in polycarbonate. Figure 6 shows the resistivity results using this equation as compared to the experimental data. In this figure, it can be seen that the model predicts that the resistivity should reach the same level for both composites since the same filler is used in

each. However, as discussed in the Results section, the polycarbonate samples do not reach the same resistivity levels as do the nylon 6,6 composites. Similar results were obtained for the other composites. This discrepancy shows that the model is inadequate for these particular systems and would require further study.

The second model applied in this study was the structure-oriented model by Weber and Kamal.[21] The specific model used was the one given in eq. (8). The appendix of this article gave instructions on how to calculate the various terms used in this model as well as what assumptions can be made. The value for θ (orientation angle) was assumed to be 33.6°, the value given in the article for injection-molded samples. Other constants were determined by using experimental data from the high-filler region. In this region, the maximum number of contacts was assumed to be 15 and this occurred at 40 wt %, consistent with the author's assumptions. The known factors include the filler resistivity from the literature[24] and the filler aspect ratio by experimental analysis. With this information, the other factors could be calculated using the equations given previously. Figure 7 shows the experimental results compared to the values predicted. It can be seen from this figure that the model closely matches the experimental data at higher-volume fractions, but is not accurate at predicting the electrical conductivity at
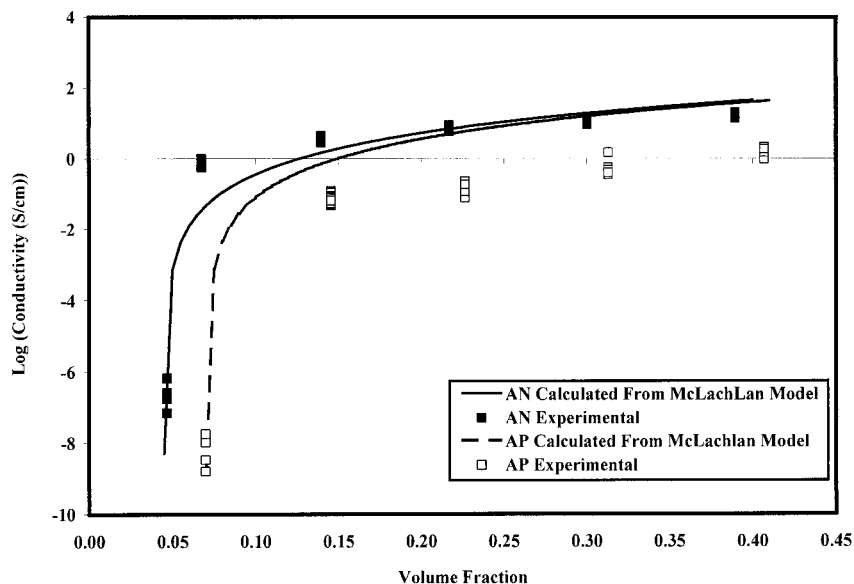
Figure 6 Experimental values for AN and AP compared to curves generated using the resistivity model by McLachlan.

low-volume fractions. The points in the high-filler region lie on the predicted curve, while the remaining points do not. Similar results and comparisons were obtained for the rest of the formulations studied. The reason that this model may not be accurate at the lower volume fractions could be that there are certain assumptions made, such as the number of interparticle contacts and the ratio of the fiber diameter to the

contact diameter, which introduce a significant amount of error in the calculations. The ratio of the fiber diameter to the contact diameter would be an extremely difficult parameter to measure, which is the reason that it is assumed. However, the assumption is that a contact area between two fibers is a circle. This is a specific case, and there could be instances where the contact area might not be a circle. Depending on the orientation an-
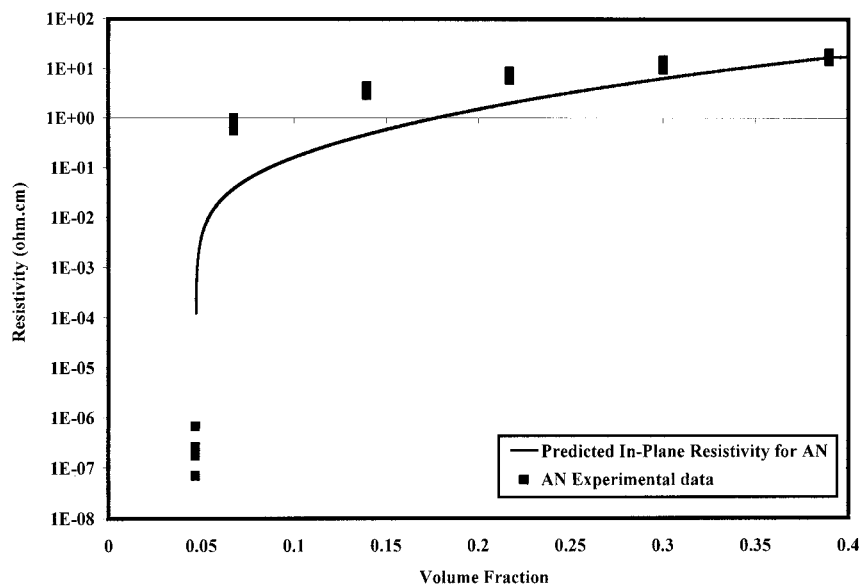

Figure 7 Experimental values for AN compared to the curves generated using the model by Weber.
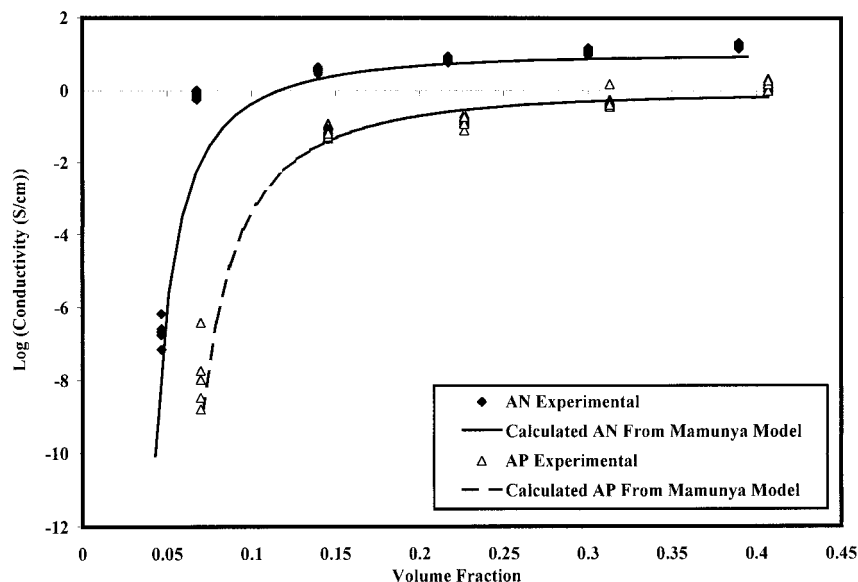
Figure 8   Experimental values for AN and AP compared to curves generated using the conductivity model by Mamunya.

gle, the contact area could be elliptical in shape, resulting in a different ratio value.

The third model, which provided some success, was the thermodynamic model proposed by Mamunya,[12,18] given previously in eq. (4). This particular model was successful because the results obtained from the calculations provided the closest match to the experimental data. To use this model, several pieces of information were required. This included the filler aspect ratio, the surface-energy values of the polymer and filler, and the conductivity of the composite at the percolation threshold and at the maximum packing fraction, F. The surface-energy values used were obtained from literature values.[27–29] Experimental data were used for the conductivity of the composite at the percolation threshold and the maximum packing fraction. Figure 8 shows the results for both chopped carbon-fiber composites, one in polycarbonate and one in nylon 6,6, with the addition of the model curves. It can be seen from this figure that the curves generated are accurate in describing the experimental results. Figure 9 shows that the results for the chopped carbon fiber and milled carbon fiber in nylon 6,6 composites were accurately modeled as well. By requiring knowledge of conductivity values at two specific points, based on experimental data, which were the percolation threshold and the maximum packing fraction, it should follow that the model accurately predicts the electrical conductivity for the entire curve. However, the two points that are required are generally the endpoints of the calculated line, and, therefore, the model should be accurate at those two volume fractions and not necessarily for volume fractions in between.

However, there are some limitations to this model: This particular model was introduced to study systems of carbon black-filled polymers. Therefore, the values of the surface energy used to generate this model were relatively low (30–55 mJ/m^2). The nickel metal coating, used in one of the fillers, has a very high surface energy similar to other metals (800–1100 mJ/m^2). Entering such a high surface-energy value into this model causes a breakdown in the system of equations, and it is unable to generate a conductivity curve. In addition, the value for the surface energy of the Thermocarb^{TM} Specialty Graphite could not be determined. A consistent, reliable surface-energy value for graphite could not be found, and, therefore, this formulation could not be modeled.

Another limitation is that this particular model does not account for the structure of the composite. Structure artifacts, such as filler orientation, can have an effect on the conductivity. If there is any orientation of the filler, it is possible that the conductivity of the composite could be different depending on the direction of measurement due to a preferred processing-dependent arrangement of the filler.
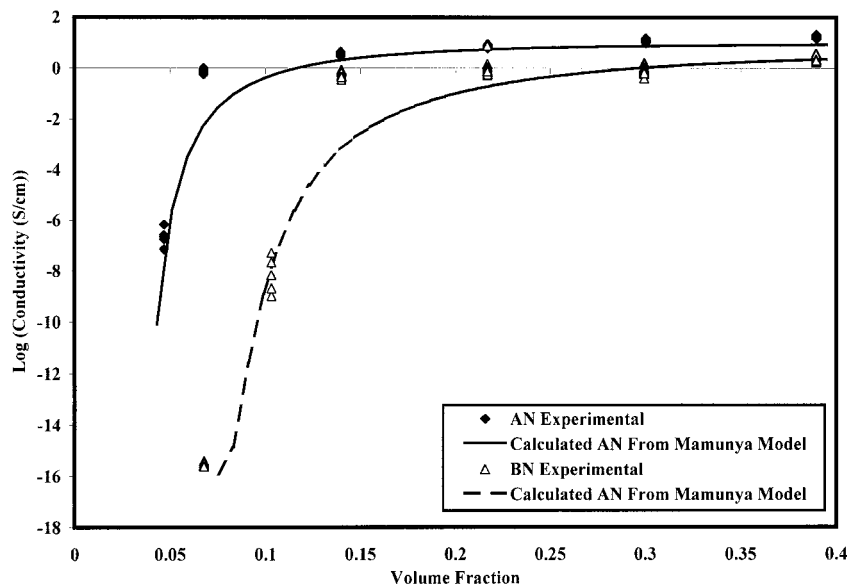
Figure 9 Experimental values for AN and BN compared to curves generated using the conductivity model by Mamunya.

CONCLUSIONS

From the work accomplished in this study, it was possible to draw several conclusions concerning the modeling of conductive composites: The conductivity of these carbon-filled composites is related to the filler aspect ratio and the surface energy of the filler and polymer. This conclusion can be drawn by examining the results for the nylon 6,6 and polycarbonate composites containing the chopped PAN-based carbon fibers and milled PAN-based carbon fibers. From these results, it can be seen that higher aspect ratios led to higher electrical conductivity values. Also, the small aspect ratio of the Thermocarb^{TM} Specialty Graphite particles, which was two, produced a low-conductivity composite, despite the high conductivity of the filler. The model by Mamunya provided the best fit of the experimental data since it incorporated the aspect ratio and surface energy into the conductivity calculations. However, it was shown that there are limitations within each model that can significantly affect the calculations. The high surface energy of nickel caused a breakdown in the model by Mamunya. In addition, in Mamunya's model, the composite structure was not considered. The curve fitting for the statistical models proved unsuccessful because the parameters that were fit did not translate to the other systems. The structure

model by Weber and Kamal relied on parameters that would be very difficult to measure experimentally and must be assumed or calculated from the experimental data. Therefore, consideration must be given to the limitations of each model as they are examined for different types of systems.

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