Development of an Additive Equation for Predicting the Electrical Conductivity of Carbon-Filled Composites

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ABSTRACT: The electrical conductivity of polymeric materials can be increased by the addition of carbon fillers. The resulting composites can be used in applications such as electrostatic dissipation and interference shielding. Electrical conductivity models are often proposed to predict the conductivity behavior of these materials. The electrical conductivity of carbon-filled polymers was studied here by the addition of three single fillers to nylon 6,6 and polycarbonate in increasing concentrations. The fillers used in this project were carbon black, synthetic-graphite particles, and milled pitch-based carbon fibers. Materials were extruded and injection-molded into test specimens, and then the electrical conductivity was measured. Additional material characterization tests included optical microscopy for determining the filler aspect ratio and orientation. The filler and matrix surface energies were also determined. An updated model developed by Mamunya and others and a new additive model (including the constituent conductivities, filler volume fraction, percolation threshold, constituent surface energies, filler aspect ratio, and filler orientation) fit the electrical conductivity results well. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2280–2299, 2003

Key words: resins; composites; modeling; polycarbonates

INTRODUCTION

The electrical conductivity of polymeric materials can be increased by the addition of carbon fillers, such as carbon fibers, carbon black, and synthetic graphite.[1–8] The resulting composites can be used in applications for which metals have typically been the materials of choice. Possible applications include electromagnetic and radio-frequency interference shielding for electronic devices and electrostatic dissipation. Electrical conductivity models are often proposed to explain and predict the conductivity behavior of these composites. The development of more accurate models would allow for more efficient material design and could reduce costly experimental work.

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, electrically insulating polymer matrix. At some critical loading, called the percolation threshold, the conductivity increases many orders of magnitude with very little increase in the filler amount. After this region of drastic increase, the conductivity levels off and approaches that of the filler material. It is at the percolation threshold that enough filler has been added so that it begins to form a continuous conductive network through the composite. This trend is displayed in Figure 1, which shows the three main regions of a typical composite electrical conductivity curve.

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 10^5 S/cm, whereas for metals, the electrical conductivity is typically 10^6 S/cm. The different forms of carbon, such as fibers and carbon black, have different inherent conductivities, and it is this value that typically controls the upper bound of the conductivity curve. In the region of higher filler amounts, the composite conductivity should level off to a value slightly lower than that of the filler.

The properties of the filler that play a significant role in determining the conductivity of the composite include the filler type, size, shape, and orientation within the matrix. Different forms of carbon generally have different microstructures and, therefore, will affect electrical conductivity in different ways. The shape of the filler has been shown to alter the conductivity. For spherical particles, smaller particles have been reported to lower the percolation threshold.[9] For fillers with an aspect ratio (length/diameter) greater than 1, larger aspect ratios and a broader range of aspect ratios have been shown to lower the percolation threshold.[10,11]
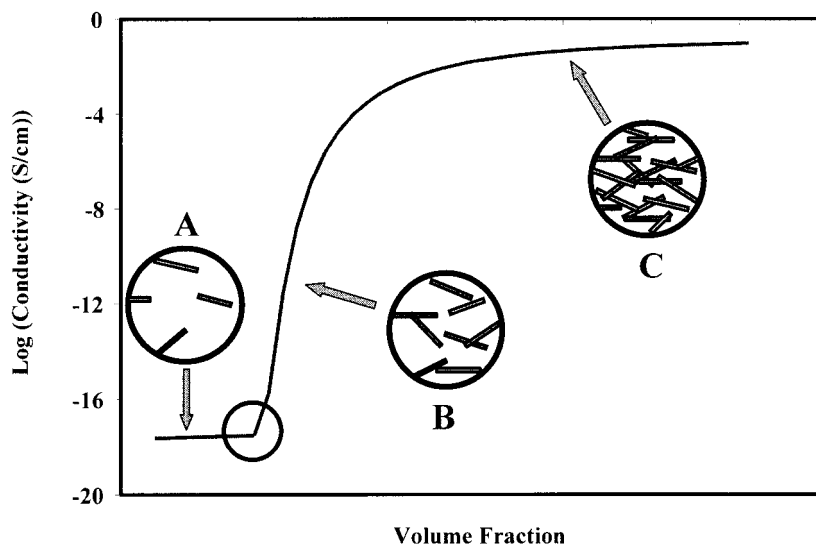
Figure 1 Dependence of the electrical conductivity on the filler volume fraction.

The surface properties of the filler and polymer also have a significant effect on the conductivity of the composite.[12] How well the polymer wets the surface of the filler can be quantified by the difference between the surface energies of the two materials. 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 coat the filler surface and that the filler distribution is more uniform (better filler dispersion). This increases the composite percolation threshold because larger amounts of filler are required before the particles come in contact with one another.[12] This can also result in increased composite electrical conductivity.[12,13]

In this project, researchers performed compounding runs followed by injection molding and electrical conductivity testing of carbon-filled resins. Two different polymers were used: nylon 6,6 and polycarbonate. The three carbon fillers investigated included an electrically conductive carbon black, synthetic-graphite particles, and a milled pitch-based carbon fiber. For each polymer, 14 formulations were produced and tested that contained various amounts of these single carbon fillers. Other material characterization tests, such as the filler aspect ratio and orientation and the constituent surface energy, were also conducted. The goal was to develop an improved electrical conductivity model for conductive composites containing short fibers or particles.

EXPERIMENTAL

Materials

For this study, two different polymers were used as matrix materials: DuPont Zytel 101 NC010, an unmodified, semicrystalline nylon 6,6, and GE Plastics Lexan HF1110-111N (denoted PC for polycarbonate), an amorphous engineering thermoplastic. The electrical conductivities of Zytel and Lexan are 10^{-15} and 10^{-17} S/cm, respectively. The properties of the polymers have been discussed elsewhere.[14–17]

Three different fillers were used in this study. The first filler material was Ketjenblack EC-600JD (denoted CB for carbon black). This is an electrically conductive carbon black available from Akzo Nobel, Inc. 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 lower amounts of carbon black. The carbon black is in the form of pellets that are 100 μm to 2 mm in size and, upon mixing into a polymer, easily separate into primary agglomerates 30–100 nm long.[18] The electrical conductivity of this carbon black is 10^2 S/cm. The second filler, denoted SG for synthetic graphite, was Thermocarb TC-300 Specialty Graphite, available from Conoco, Inc.[19] This material is a high-quality synthetic graphite used because of its high thermal and electrical conductivity. It was milled to an average particle size of approximately 70 μm and an aspect ratio of about 1.7, as determined by optical microscopy. The electrical conductivity of this material is approximately 10^5 S/cm.[19] The third filler used in this project was BP/Amoco ThermalGraph DKD X petroleum pitch-based carbon fibers, which were milled to 200 μm long; it was denoted CF for carbon fiber. This particular fiber was used because it improves the thermal and electrical conductivity and tensile strength of conductive resins. The electrical conductivity of this fiber is approximately 3333 S/cm.[20] Additional properties of these fillers have been discussed elsewhere.[15,18–20]

Composites containing various amounts of a single filler were produced. The following loading levels

were used in both polymers: (1) Ketjenblack EC-600JD, 2.5, 4.0, 5.0, 6.0, 7.5, and 10.0 wt %; (2) Thermocarb TC-300 Specialty Graphite, 10.0, 15.0, 20.0, 30.0, and 40.0 wt %; and (3) ThermalGraph DKD X, 5.0, 10.0, 15.0, 20.0, 30.0, and 40.0 wt %.

Test specimen fabrication

For this entire project, the fillers were used as received. Zytel 101 NC010 and Lexan HF 1110-111N were dried in an indirectly heated dehumidifying drying oven and then were stored in moisture barrier bags.

The extruder used was an American Leistritz Extruder Corp. model ZSE 27. It had a 27-mm corotating intermeshing twin screw with 10 zones and a length/diameter ratio of 40. The screw design was chosen for the maximum possible conductivity. Therefore, a minimum amount of filler degradation was desired, with the fillers still being well dispersed in the polymers. The polymer pellets (Zytel or Lexan) were introduced in zone 1. The first side stuffer, used to introduce carbon black and Thermocarb TC-300 Specialty Graphite into the polymer melt, was located at zone 5. The second side stuffer was located at zone 7 and was used to introduce the carbon fiber into the polymer melt. Four Schenck AccuRate gravimetric feeders were used to accurately control the amount of each material added to the extruder.

After passing through the extruder, the polymer strands (3 mm in diameter) entered a water bath and then a pelletizer that produced pellets nominally 3 mm long. After compounding, the pelletized composite resin was dried and then stored in moisture barrier bags before injection molding.

A Niigata model NE85UA$_4$ injection-molding machine was used to produce test specimens. It had a 40-mm-diameter single screw with a length/diameter ratio of 18. A four-cavity mold was used to produce 3.2-mm-thick ASTM type I tensile bars (end-gated) and 6.4-cm-diameter disks. The electrical conductivity of all the molded formulations were determined.

In-plane electrical conductivity test method

The volumetric in-plane (longitudinal) electrical conductivity was measured on all samples with a conductivity greater than 10^{-4} S/cm. Test specimens from the center gauge portion of a tensile bar, as shown in Figure 2(A), were surface-ground and then cut into specimens 2 mm wide, 2 mm thick, and 25.4 mm long. For each formulation, 6 specimens in all were cut from a single tensile bar, and four tensile bars were typically used to obtain a total of 24 test specimens. These samples were then tested with a four-probe technique. This technique measures conductivity by applying a constant current (typically 5–10 mA) and measuring the voltage drop over the center 6 mm of the sample
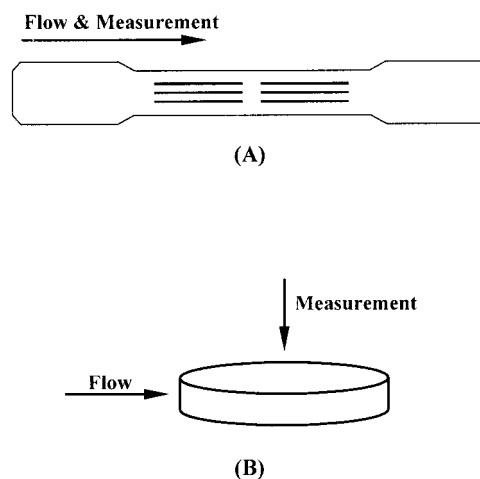
Figure 2 Diagram of injection-molded test specimens illustrating the directions of the flow and electrical conductivity measurements for (A) in-plane and (B) through-plane electrical conductivity specimens.

(ΔV).[21] A Keithley 224 programmable current source and a Keithley 182 digital sensitive voltmeter were used. The following equation was used to calculate the electrical conductivity:

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

where EC is the electrical conductivity, w is the width, t is the thickness, L is the length over which ΔV is measured (0.6 cm), and i is the current.

Through-plane electrical conductivity test method

For samples with a conductivity of less than 10^{-5} S/cm, the transverse, or through-plane, volumetric electrical conductivity was determined according to ASTM D 257 with a Keithley 6517A electrometer/high-resistance meter and a Keithley 8009 resistivity test fixture.[22] Keithley 6517 Hi-R test software was used to automate the conductivity measurement. The samples tested were molded 3.2-mm-thick, 6.4-cm-diameter disks, as shown in Figure 2(B). In this method, a constant voltage, typically 10 or 100 V, was applied to the test specimen, and the resistivity, the inverse of conductivity, was measured. For each formulation, a minimum of six specimens were tested. For both electrical conductivity test 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 for 24 h and then tested.

Surface energy test method

Surface energies for the three fillers were measured with the Washburn adsorption method.[23] The two components of the total surface energy, a polar com-

ponent and a dispersive component, were determined.[24] This analysis was performed with a Kruss K12 processor tensiometer with an FL12 powder cell accessory and was carried out by Kruss Laboratory Services in Charlotte, NC.[25] The total, polar, and dispersive components of the polymer surface energy were determined in the melt phase (to simulate extrusion and injection molding) with the pendant drop technique by Kruss Laboratory Services.[25] A Kruss DSA10 drop shape analysis system was used.

X-ray photoelectron spectroscopy (XPS)

XPS was used to determine the surface compositions of the various carbon fillers. Because each element has a unique set of binding energies, XPS can determine the elements present in the top 50–100 Å of the surface of a particular sample. For the completion of this analysis, a PerkinElmer PHI 1600 XPS system was used in an ultrahigh vacuum chamber held at pressures of 1×10^{-9} Torr. The Thermocarb TC-300 Specialty Graphite and the Ketjenblack EC-600 JD were pressed into 1-cm-diameter wafers with a hydraulic press. The ThermalGraph DKD X pitch-based carbon fiber was mounted on the sample holder with double-sided copper tape.

Once the samples were mounted on the sample holder, they were inserted into a prepump chamber, and the pressure was pumped down to the 10^{-8} Torr range. The sample was then inserted into the main vacuum chamber, and the pressure was reduced to below 5×10^{-8} Torr. The voltage was slowly increased to 15 kV, and the Mg X-ray source was increased to 300 W. The sample was then irradiated with X-rays, and the energy of the detected electrons was collected.

Microscopy methods

To determine the length, aspect ratio, and orientation of the carbon fibers and synthetic-graphite particles, we used microscopic methods. For the orientation measurements, an in-plane electrical conductivity sample, cut from the center portion of the tensile specimen, as shown in Figure 2(A), was cast in two-part epoxy in a position such that the direction of flow induced in the injection-molding machine, which was equivalent to the direction of the conductivity measurement, would be viewed. So that the through-plane samples could be viewed, the center portion was cut out of the disk, as shown in Figure 2(B), and was set in the epoxy such that the direction of the electrical conductivity measurement, perpendicular to the direction of flow induced in injection molding, would be viewed. The sample was then polished with a Buehler Ecomet 4 polishing wheel fitted with an Automet 2 polishing head. An Olympus BX60 transmitted light microscope at a magnification of 200× was used to obtain images of the polished surface.

To obtain the length and aspect ratio of the fillers, we used solvent digestion to remove the polymer matrix from the filler. At 23°C, formic acid was used to dissolve the nylon 6,6, and methylene chloride was used to dissolve the polycarbonate. The particles or fibers were then dispersed onto a microscope slide and viewed with an Olympus SZH10 reflected light microscope at a magnification of 60×. Digital images were taken of the filler, as well as the polished composite samples, and were then analyzed with Adobe Photoshop version 5.0 installed with the Image Processing Tool Kit. Because of the extremely small size of the carbon black (the aggregates were 30–100 nm in size), the length, aspect ratio, and orientation of the carbon black were not measured.

RESULTS

Electrical conductivity

The electrical conductivity results for carbon-black-filled composites can be found in Figure 3. In this figure and in all the other figures showing the results, all of the data points have been plotted to show the actual spread in the experimental data. This figure shows that carbon black is effective at increasing the conductivity of the polymer at low filler loadings. At no filler loading, the neat nylon had an electrical conductivity of approximately 8×10^{-15} S/cm (the vendor literature states 10^{-15} S/cm), and the neat polycarbonate had an electrical conductivity of approximately 1×10^{-17} S/cm (the same as the value in the vendor literature). At the high filler volume fractions, the carbon black produced a composite conductivity of approximately 1×10^{-1} S/cm in both polycarbonate (6.9 vol %) and nylon (6.6 vol %).

It can also be seen in this figure that the data curves follow the basic form characteristic of percolation conductivity, as shown in Figure 1. That is, at low filler loadings, the conductivity remains at very low levels, and at the percolation threshold, the conductivity increases dramatically and then begins to level out again at a value many orders of magnitude higher. In the case of the carbon-black composites, the percolation threshold can be approximated to be at a volume fraction of 0.025, or 2.5 vol %, for both polycarbonate and nylon formulations.

Figure 4 displays the electrical conductivity results for the composites filled with the synthetic graphite. The data in this figure show that the synthetic graphite produced a composite conductivity of approximately 2×10^{-3} S/cm at a volume fraction of 0.25 for nylon and approximately 2×10^{-2} S/cm for polycarbonate at a volume fraction of 0.26. From the data in this figure, the percolation threshold, or the point at which the composite electrical conductivity begins to dra-
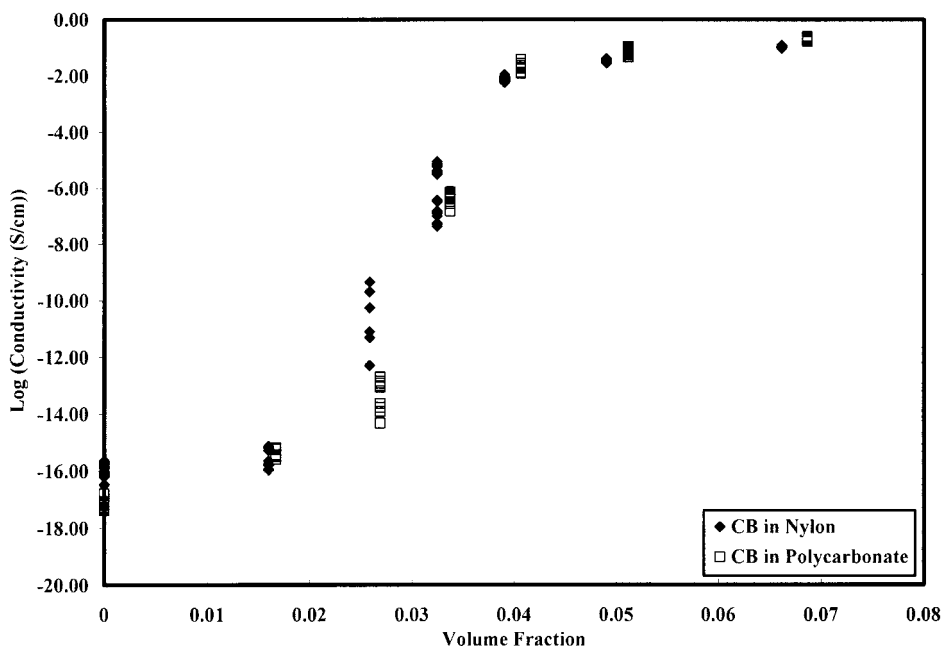
Figure 3   Electrical conductivity results for carbon-black composites.

matically increase, can be approximated to be 11 vol % for both nylon and polycarbonate.

The electrical conductivity results for the pitch-based carbon fibers can be found in Figure 5. The carbon-fiber-filled composites had an electrical conductivity of approximately 1×10^{-1} S/cm for nylon 6,6 (volume fraction of 0.26) and polycarbonate (volume fraction of 0.27). From these data, the percolation threshold can be approximated to be 9.0 vol % for both nylon 6,6 and polycarbonate-based composites.

Table I summarizes the values obtained for the percolation threshold and the electrical conductivity at the highest volume fraction composite. One column in this table shows the base 10 logarithm of the electrical conductivity. With the logarithm, conductivity values can be easily compared in terms of orders of magnitude. A decreasing negative number in these results indicates an increasing electrical conductivity. This table shows that composites containing carbon black had the lowest percolation threshold. This is due
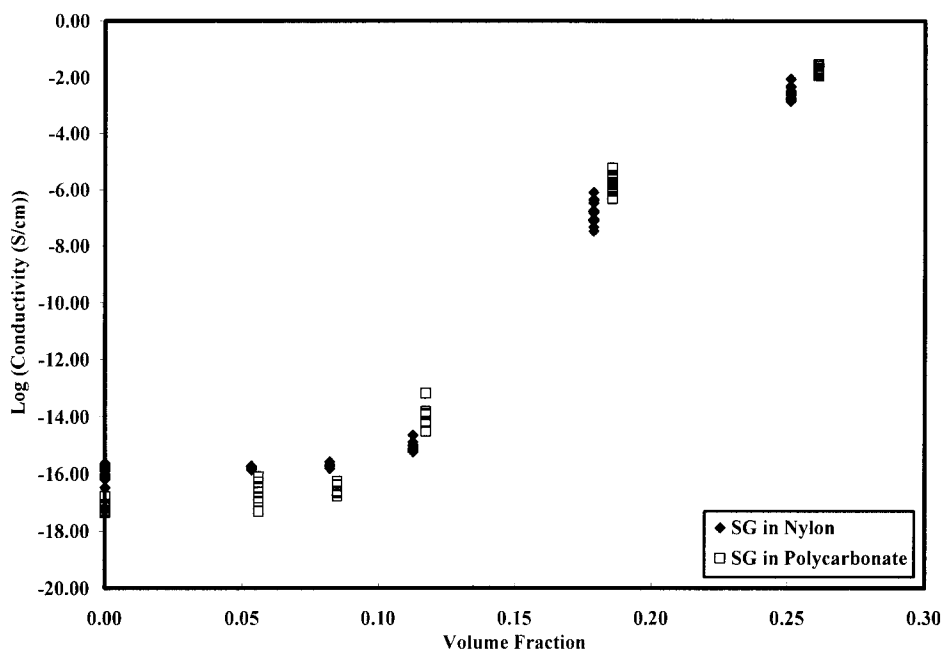
Figure 4   Electrical conductivity results for synthetic-graphite composites.
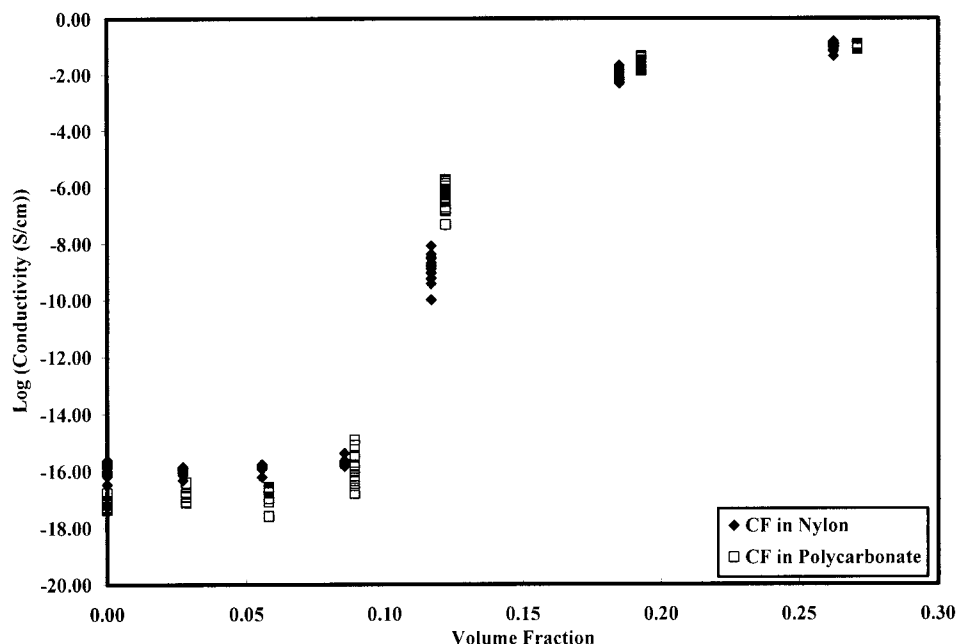
Figure 5 Electrical conductivity results for carbon-fiber composites.

mainly to the small size and high surface area of the carbon-black particle. Additionally, composites consisting of 10 wt % carbon black (6.9 vol %) in polycarbonate had the highest electrical conductivity of 0.20 S/cm (corresponding to a value of −0.69 for the base 10 logarithm). The table also shows that the carbon-fiber composites had a higher electrical conductivity and lower percolation threshold than the synthetic-graphite-filled composites. This difference could be due to several different factors, including the aspect ratio and orientation of the fillers. Therefore, the results from the other experimental techniques needed to be analyzed.

Surface energy and XPS

Table II[25] gives the total, polar, and dispersive surface energy components for all the materials used. The total surface energy for nylon 6,6 was 45.92 mJ/m^2 in the melt phase. Polycarbonate had a total surface energy of 38.05 mJ/m^2 in the melt phase. The total

surface energy of the carbon black was measured to be 21.77 mJ/m^2. The carbon fiber had a total surface energy of 22.23 mJ/m^2, and the synthetic graphite had a total surface energy value of 24.00 mJ/m^2. Because all the filler surfaces were composed of essentially pure carbon, one would expect the surface energy results for these fillers to be similar.

The surface polarity values (polar surface energy component/total surface energy) are also given in Table II.[25] These results can be used to determine which polymer would provide for more complete dispersion with each of the fillers. Materials that have similar surface polarity values provide improved dispersion in composites.[26] The results in Table II indicate that the polycarbonate matrix had a surface polarity more comparable to that of the carbon fillers and, therefore, should provide for a more complete dispersion of each of the carbon fillers versus nylon 6,6.

Results from the XPS analysis for all three fillers used are also in Table II. Only two elements were

TABLE I
Comparison of Percolation Threshold and Highest Electrical Conductivity Values

Composite	Percolation threshold (volume fraction)	Highest volume fraction	Conductivity at highest volume fraction (S/cm)	Log(conductivity) at highest volume fraction (S/cm)
Carbon black/nylon 6,6	0.025	0.066	0.11	−0.97
Synthetic graphite/nylon 6,6	0.105	0.251	0.0023	−2.63
Carbon fibers/nylon 6,6	0.090	0.262	0.10	−1.00
Carbon black/polycarbonate	0.025	0.069	0.20	−0.69
Synthetic graphite/polycarbonate	0.105	0.261	0.017	−1.76
Carbon fiber/polycarbonate	0.090	0.271	0.095	−1.02

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TABLE II
Surface Energy and XPS Results[25]

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Material	Polar component (mJ/m^2)	Dispersive component (mJ/m^2)	Total surface energy (mJ/m^2)	Surface polarity (%)	Oxygen on filler surface (atomic %)
Zytel 101 NC010	17.24	28.68	45.92	37.5	—
Lexan HF1110-111N	8.55	29.50	38.05	22.5	—
Carbon black	2.18	19.59	21.77	10.0	1.3
Synthetic graphite	3.99	20.01	24.00	16.6	1.8
Pitch-based carbon fiber	5.47	16.76	22.23	24.6	3.7

present on the filler surface, carbon and oxygen. This table shows that, as expected, all the fillers consisted mainly of carbon. Also as expected, as the amount of oxygen present on the filler surface increased, the polar component of the surface energy increased.

Length and aspect ratio

The average lengths of the carbon fibers and graphite particles after extrusion and injection molding are displayed in Figure 6, and the aspect ratio results are given in Figure 7. As stated previously, this test was only performed on the carbon fiber and synthetic-graphite particles, as the carbon black was too small to measure with this technique. These figures show two distinct results: one for the carbon fibers and another for the synthetic-graphite particles.

Figure 6 shows that there was significant degradation of the carbon fibers as a result of the composite processing. The average length of the carbon fibers before processing was approximately 170 μm, similar to the value of 200 μm reported by the vendor.[20]

Lengths were significantly reduced to an average value of approximately 90–100 μm in the injection-molded samples, with a diameter of 10 μm. These length results are comparable to those reported by Bigg,[27] who showed that carbon-fiber/nylon 6,6 composites had fiber lengths of approximately 130 μm after extrusion and injection molding. Figure 7 shows that the aspect ratio of the carbon fibers were reduced from an original value of 16.8 to values ranging between 9 and 10.5 after the extrusion and injection-molding processes. However, after the initial fiber degradation, it appears that there was no significant change in the lengths and aspect ratios as the filler was increased. For example, the length of the fibers in the 5 wt % fiber in the nylon 6,6 formulation was 90 μm. The length of the fibers from the 40 wt % in the nylon formulation was approximately 95 μm. The same general trend was true for the polycarbonate results.

Figures 6 and 7 also show the lengths and aspect ratios of the synthetic-graphite particles (Thermocarb Specialty Graphite). These figures show that the length and aspect ratio of the synthetic-graphite par-
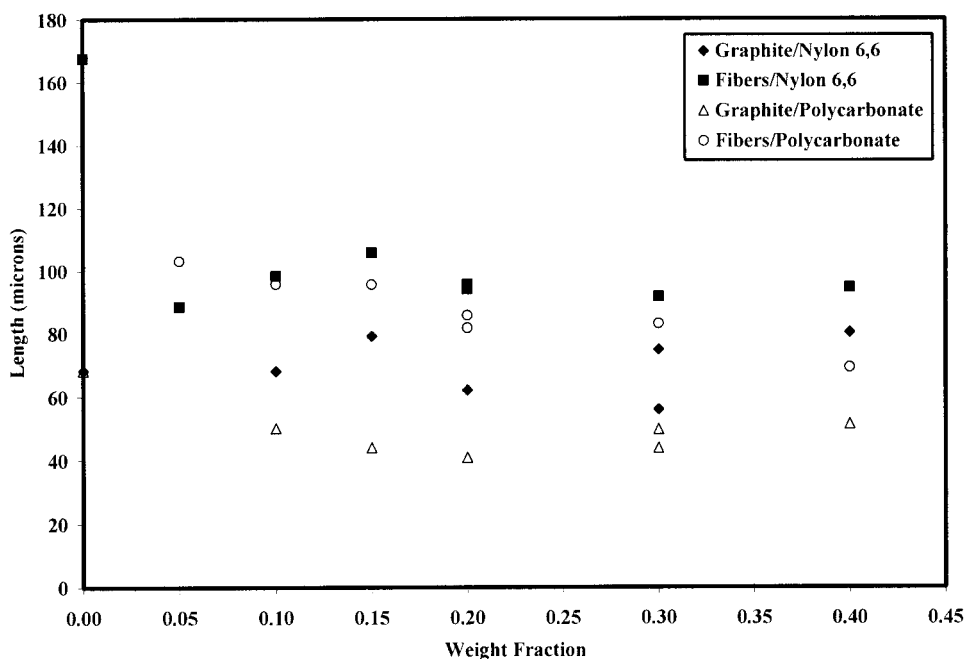

Figure 6 Mean lengths of carbon fibers and synthetic-graphite particles in injection-molded samples.
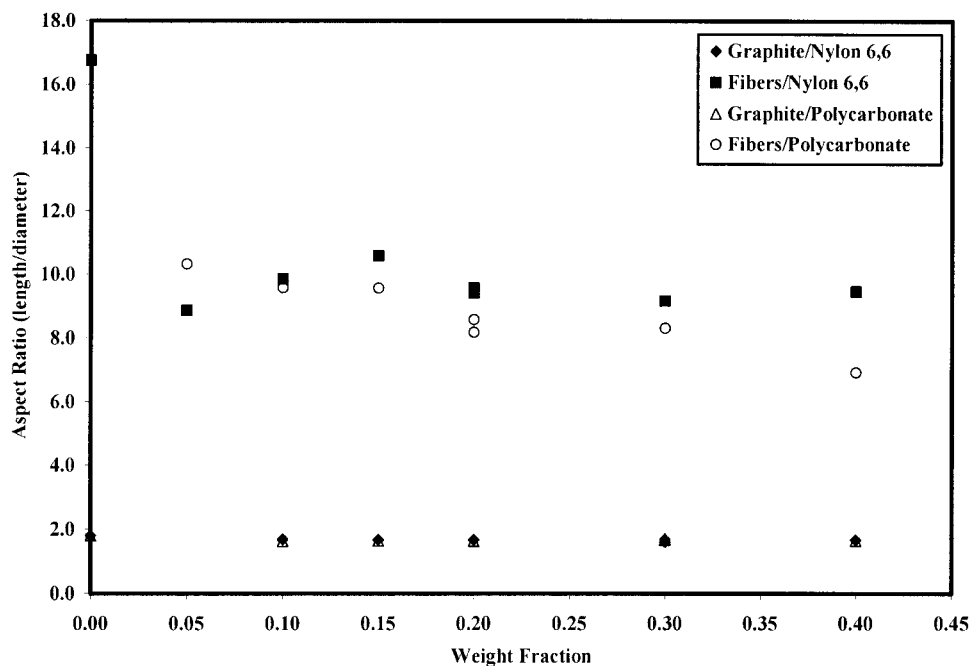
Figure 7 Mean aspect ratio results for carbon fibers and synthetic-graphite particles in injection-molded samples.

ticles in the composite specimens remained similar to those of the as-received material. This result was likely due to the relatively small length and aspect ratio of the as-received Thermocarb Specialty Graphite. The as-received synthetic graphite had a mean length of 68 μm and a mean aspect ratio of 1.8. The aspect ratio decreased slightly from 1.80 to approximately 1.65, and the length also decreased from 70 μm to approximately 40 to 50 μm. Moreover, Figure 7 shows that there was no substantial difference in the aspect ratios of the particles with increasing weight percentages of the fillers.

Orientation in in-plane conductivity samples

The purpose of this portion of the study was to determine if there was any orientation of the fillers as a result of injection molding and what effect this would have on the electrical conductivity results. It has been discussed previously that the orientation of particles in a matrix can increase the conductivity when it is measured in the direction of the alignment. For this reason, evidence of any alignment of the fillers, specifically an angle of orientation, should be included in any electrical conductivity model. Therefore, the orientation of the particles and fibers was measured with polished composite samples by optical microscopy.

The angle of interest in these measurements was the deviation of the filler away from the angle of the electrical conductivity measurement. In the case of the in-plane electrical conductivity samples, it was anticipated that the fillers would orient in the direction of the polymer flow occurring during injection molding, which was the same as the direction of measurement.

This is depicted in Figure 2(A). This figure shows the location of the tensile bar from which the in-plane conductivity samples were cut and how the material flowed into the end-gated mold. For these measurements, all of the angles were between 0 and 90°.

Figure 8 shows the orientation results for an in-plane conductivity sample containing 30 wt % carbon fiber in nylon 6,6. The orientation angle results are accompanied by the figure from which the angle was measured. The angles were measured with respect to the direction of flow and measurement, which is denoted by the arrow at the bottom of the figure. Three samples were measured, and the results were then averaged together so that one angle was obtained for each formulation. An angle of 0° signified that the filler was aligned in the direction of flow into the mold, which was also the direction of conduction for the in-plane electrical conductivity samples. An angle of 90° meant that a filler was perpendicular to the direction of flow and measurement.

The results shown in Figure 8 are typical for all of the carbon-fiber-filled composites, both in nylon 6,6 and polycarbonate. Overall, the average value for the orientation angle in the 30 wt % carbon-fiber composites was 25.0°, with a median value of 17.2° and a standard deviation of 23.7°. These results were obtained by the measurement of 6789 particles in the composite. These results, when combined with the histogram, confirmed that the majority of the carbon fibers were oriented in the flow, or in-plane, direction, which was also the direction of measurement (more fillers found close to the 0° orientation angle). Additionally, these results agree with those of other researchers who obtained similar distributions of orien-
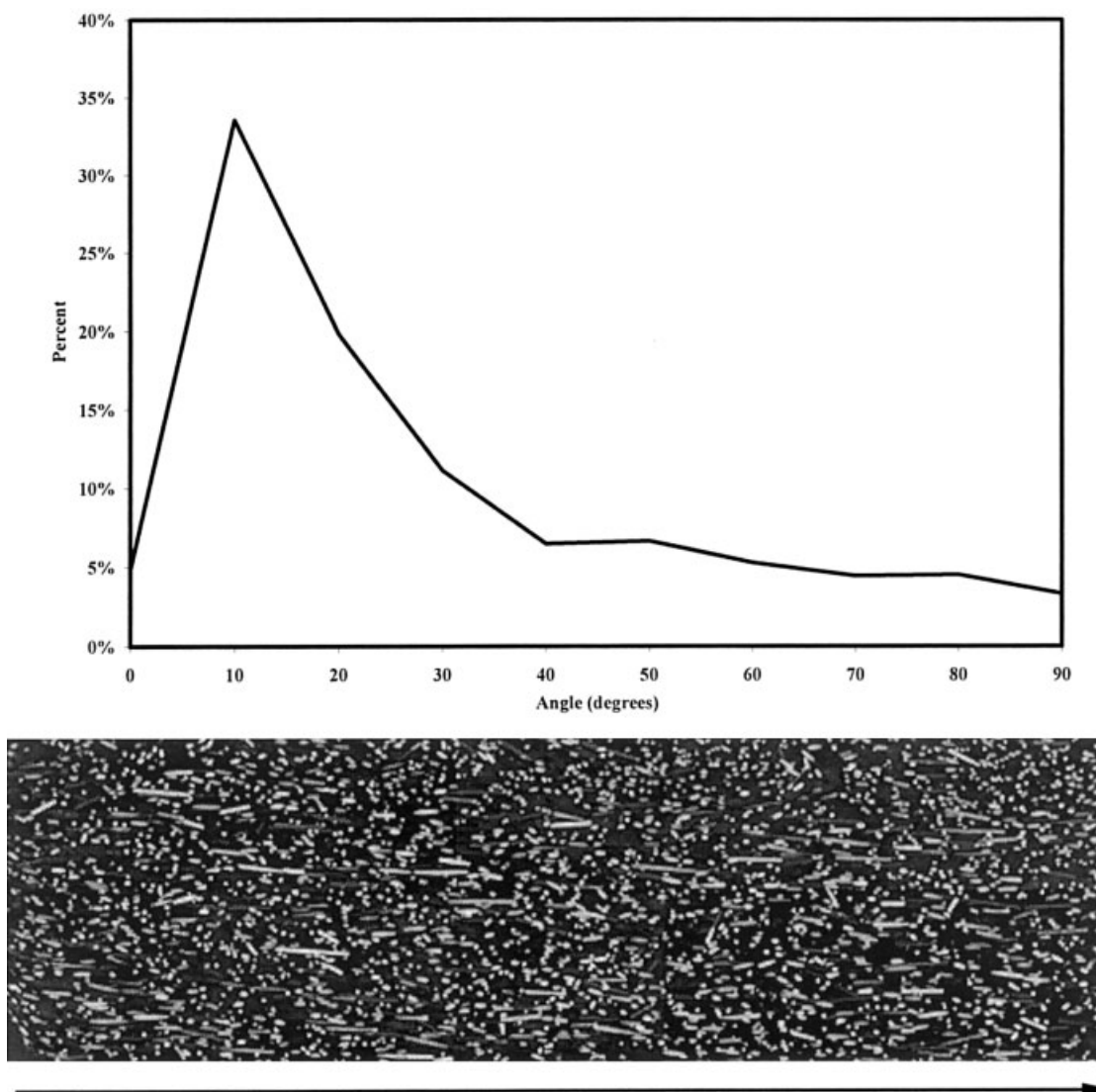
Figure 8 Orientation results and composite image for an in-plane conductivity sample containing 30 wt % carbon fiber in nylon 6,6.

tation angles.[28,29] However, the orientation angle was lower than the value of 33.6° obtained by Weber and Kamal[30] for injection-molded samples.

The orientation results for an in-plane conductivity sample that was 40 wt % synthetic graphite in nylon 6,6 are shown in Figure 9. This figure shows that, in general, the orientation for the graphite particles in the in-plane direction was slightly more random than that of the carbon fibers. This was most likely due to the smaller aspect ratio of the graphite particles, which varied between 1.61 and 1.68, versus a range of 9.0– 10.5 for the fibers. The histogram shows that the variation in the orientation angle was slightly wider in the graphite particles as well. For this formulation, the overall average angle was 29.7°, with a median of 24.37° and a standard deviation of 26.11° measured on 2480 particles. As in the previous figure, the arrow at the bottom shows the direction of the conductivity measurement and flow. The orientation histogram

and the composite image for this sample were typical for the synthetic-graphite-filled composites.

Orientation in through-plane conductivity samples

In the through-plane (transverse) electrical conductivity test samples, the direction of flow into the mold was perpendicular to the direction of the conductivity measurement, as shown in Figure 2(B). The orientation angle was also measured optically for these samples. For the formulation containing 10 wt % carbon fiber in nylon 6,6, the mean orientation angle was 71.6°, with a median of 81.1° and a standard deviation of 22° (2058 fibers measured). In this case, the orientation angle was closer to 90°, indicating that the fibers were primarily oriented transverse to the conductivity measurement direction. The same conclusion can also be drawn for the composites containing synthetic graphite. For the 10 wt % synthetic graphite in nylon
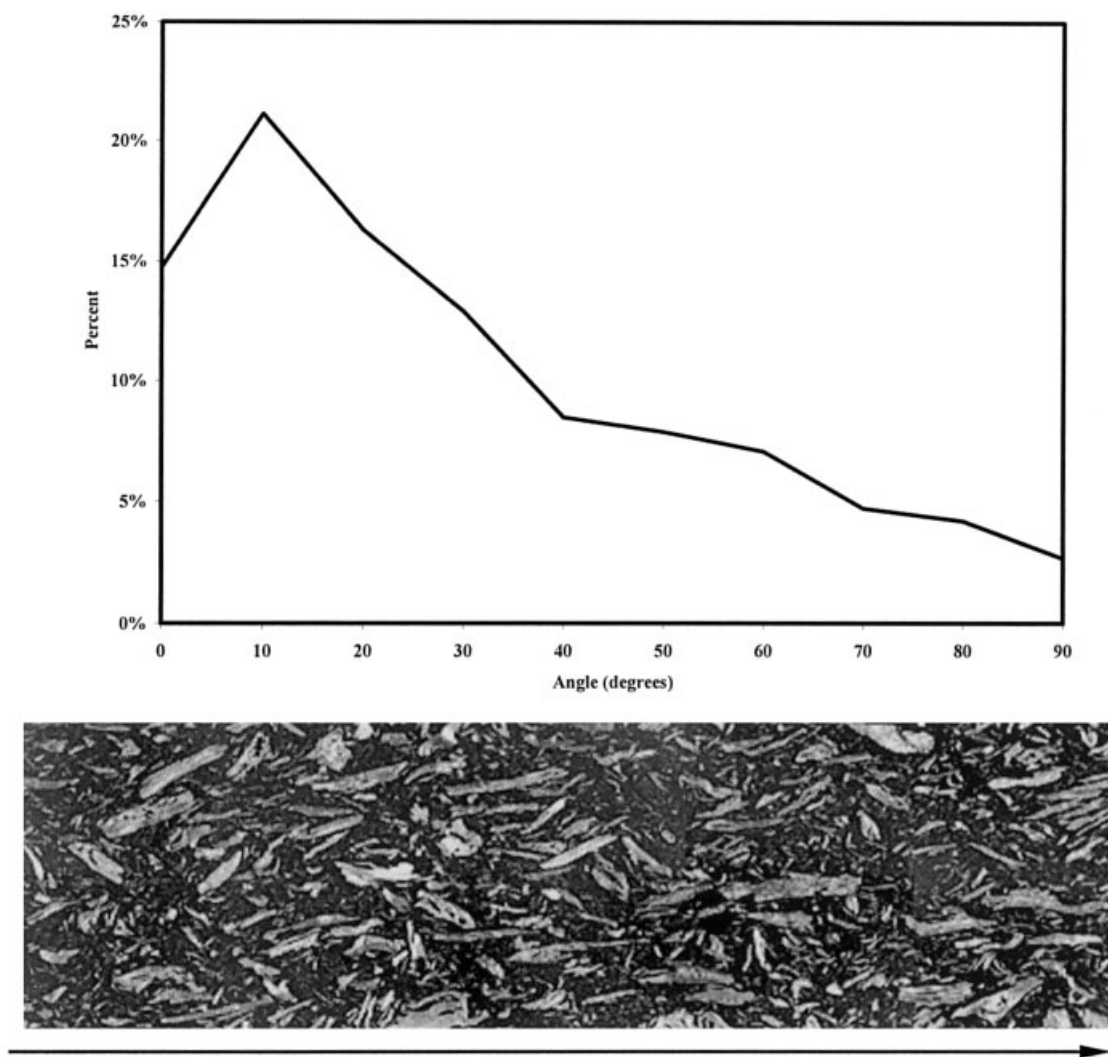
Figure 9 Orientation results and composite image for an in-plane conductivity sample containing 40 wt % synthetic graphite in nylon 6,6.

6,6, the mean orientation angle was 58.7°, with a median of 65.3° and a standard deviation of 24° (733 particles measured). Additional through-plane conductivity orientation results are reported elsewhere.[31]

MODELING BACKGROUND

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.[32] A brief description of each class of models is given here, and the reader is referred to the article by Lux, or to previous work by us,[14] for further details on specific models within each class.

Statistical percolation models

Most of the models found in the literature are of the statistical percolation type. These models typically

predict the conductivity according to the probability of particle contacts within the composite. Two of the early percolation models often referenced were originally proposed by Kirkpatrick[33] and Zallen.[34] A finite regular array of points, such as face-centered cubic or body-centered cubic, and bonds (between the 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 system. 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:

$$\sigma = \sigma_f(\phi - \phi_c)^s \qquad (2)$$

where σ is the composite electrical conductivity, σ_f is the electrical conductivity of the filler, ϕ is the filler

volume fraction, ϕ_c is the percolation threshold volume fraction, and s depends on the lattice dimensions. This particular model was not completely accurate in calculating the electrical conductivity. However, it became the basis for many of the later conductivity models.

Thermodynamic models

Mamunya et al.[12,35] 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 the filler and polymer surface energies and the 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 as follows:

$$\log \sigma = \log \sigma_c + (\log \sigma_F - \log \sigma_C)\left(\frac{\phi - \phi_c}{F - \phi_c}\right)^k \quad (3)$$

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

$$K = A - B\gamma_{pf}$$

where σ_c is the electrical conductivity at the percolation threshold; σ_F is the composite electrical conductivity when $\phi = F$; F is the maximum packing volume fraction; γ_{pf} is the interfacial surface tension; and A, B, and n are constants.

The value k is dependent on the filler volume fraction, percolation threshold, and interfacial tension, as calculated by the Fowkes[24] equation:

$$\gamma_{pf} = \gamma_p + \gamma_f - 2(\gamma_p^d \gamma_f^d)^{0.5} \quad (4)$$

where γ_{pf} is the interfacial surface tension; γ_p is the polymer total surface energy, which is equal to the sum of the polymer dispersive and polar surface energies; γ_f is the filler total surface energy, which is the sum of the filler dispersive and polar surface energies; γ_p^d is the polymer dispersive surface energy; and γ_f^d is the filler dispersive surface energy.

When Mamunya et al.[12,35] applied eq. (4) to their system, they used a modified form of the Fowkes equation to determine γ_{pf}:

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

This model produced a good agreement between the calculated values and the experimental data for a number of different polymers filled with carbon black.[12]

Geometrical percolation models

According to Lux,[32] 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, whereas 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 lengths of the sintered insulating particles.

A well-known model in this class is the one proposed by Malliaris and Turner.[36] 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 diameters of the particles, the probability for the occurrence of long bands of conductive particles on the surfaces of insulating particles, and the arrangement of the conductive particles on the surfaces of the insulating particles. After experimental results from this project were compared, 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 to the flow through the nozzle and the mold. The 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.

Weber and Kamal[30] proposed two models (end-to-end and fiber-contact) 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 connected end-to-end in a polymer matrix and that the fibers were aligned in the direction of the electrical conductivity test. Another model was proposed that took into account the fiber–fiber contacts, fiber length, and alignment of the fibers at an angle θ to the electrical conductivity test direction. The resulting equation for the contact can be given as follows:

$$\rho_{c,\text{long}} = \frac{\pi d^2 \rho_f X}{4 \phi_p d_c \ell \cos^2\theta}$$

$$X = \frac{1}{0.59 + 0.15m}$$

$$\phi_p = \beta\phi$$

$$\beta = \frac{\phi - \phi_c}{\phi_t - \phi_c} \tag{6}$$

where $\rho_{c,\text{long}}$ is the longitudinal composite electrical resistivity, ρ_f is the fiber electrical resistivity, X is the function of the number of contacts, d_c is the diameter of the circle of contact, d is the fiber diameter, ℓ is the fiber length, m is the number of contacts, ϕ_p is the volume fraction of fibers participating in conductive strings, θ is the angle of orientation, and ϕ_t is the threshold value at which all fibers participate in strings.

Although some structure-oriented models can accurately predict conductivity, a major limitation to all models in this class is that they neither account for nor predict the surface energy interactions that have been shown to have a significant effect on the conductivity of the composite. The thermodynamic model by Mamunya et al.[12] shows that the conductivity is related to the surface interactions of the polymer and filler.

Previous work by the authors of this article

In previous work of ours,[14] electrical conductivity models that account for the different factors were evaluated by a parametric study and then compared to experimentally determined electrical conductivity results. This work was performed on nylon 6,6- and polycarbonate-based composites containing PAN-based (200-μm milled and 3.2-mm chopped) carbon fibers, synthetic graphite, and nickel-coated PAN-based carbon fibers as single fillers. From the work accomplished in the previous study, it was possible to draw certain conclusions concerning the modeling of conductive composites. The conductivity of the carbon-filled composites studied was related to the filler aspect ratio and the surface energy of the filler and polymer. The results showed that higher aspect ratios led to higher electrical conductivity values. The results also provided an initial confirmation of Mamunya et al.'s work[12] that the surface energy was a significant factor in composite electrical conductivity. From the models evaluated in the previous work,[14] the model by Mamunya et al.[12] provided the best fit of the experimental data because it incorporated the aspect ratio and surface energy into the conductivity calculations. However, there are limitations within each model that can significantly affect the calculations. For example, in Mamunya et al.'s model, the composite

structure is not considered. The curve fitting for the statistical models proved unsuccessful because the parameters that were fit did not translate well to other systems. The structure model by Weber and Kamal[30] relied on parameters that would be very difficult to measure experimentally and must be assumed or calculated from experimental results. Therefore, consideration must be given to the limitations of each model as they are examined for different types of systems.

MODELING ANALYSIS

For the modeling analysis for this project, Microsoft Excel 2000 was used to compare the experimental results and the calculated values. By using spreadsheet software, we could immediately observe how changes in the different constants affected the shape and position of the conductivity curve. Additionally, the solver add-in could be used to minimize the sum of squares of the residuals between the actual and calculated values. The constants for the models were first estimated by the minimization of the sum of squares of the residuals between the actual and calculated values. Then, in an effort to obtain constants that were the same for all materials, we visually fit these constants to the data because all the data were plotted graphically.

Updated Mamunya model

It was determined in the previous study[14] that the model proposed by Mamunya et al.,[12] which calculates the composite electrical conductivity from the constituent surface energy, the maximum packing fraction (a function of the aspect ratio), and the conductivity at the percolation threshold, was the best at calculating electrical conductivity values. First, the data from this project were analyzed with the original model proposed by Mamunya et al. For all filler volume fractions less than the percolation threshold, the composite conductivity was approximated to be that of the pure polymer conductivity. Equation (7) shows the equations used for all filler volume fractions greater than the percolation threshold. The values for the constants A, B, and n were determined by Mamunya et al. and have been inserted into eq. (7):

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

$$k = \frac{K\phi_c}{(\phi - \phi_c)^{0.75}}$$

$$K = 0.28 - 0.036\gamma_{pf} \tag{7}$$

Equation (5) was used to determine γ_{pf}. For the carbon-black composites, eq. (8) was used to determine F, the maximum packing fraction. This equation was

Material	Log(conductivity) (S/cm)	As-received aspect ratio	Orientation angle (°)	Filler vibrated bulk density (g/cc)	Material density (g/cc)	F vol. fraction
Zytel 101	−15.97	—	—	—	1.14	—
Lexan	−17.16	—	—	—	1.20	—
Carbon black	2.00	—	45	0.1082	1.80	0.060
Synthetic graphite	5.00	1.80	25	0.5330	2.24	0.238
Carbon fiber	3.52	16.75	25	0.4840	2.15	0.225

developed by Mamunya et al. for carbon-black composites:

$$F = 0.65\phi_c^{1/3} \tag{8}$$

Because carbon fiber is very different in shape from carbon black, eq. (9) was used to determine F. This incorporates the filler aspect ratio (a) and was proposed by the same authors:[35,37]

$$F = \frac{5}{\dfrac{75}{10 + a} + a} \tag{9}$$

For synthetic graphite, another approach was used to obtain F because using eq. (9) resulted in a value of F of 0.61, which was too high (realistic values of F are typically less than 0.3). Instead, F was determined experimentally. Therefore, 10 g of synthetic graphite was placed into a 25-mL graduated cylinder and vibrated at 50 Hz for 5 min. The following equation was used to calculate F:

$$F = \frac{\text{Mass of filler}}{\text{Vibrated volume} \cdot \text{specific gravity of filler}} \tag{10}$$

On the basis of the analysis of the original model, possible improvements to the Mamunya model were investigated. One improvement was an alternate version of the Fowkes equation, as updated by Owens and Wendt[38] to fully account for the polar and dispersive surface energy components of the polymers and fillers:

$$\gamma_{pf} = \gamma_p + \gamma_f - 2(\gamma_p^d \cdot \gamma_f^d)^{0.5} - 2(\gamma_p^p \cdot \gamma_f^p)^{0.5} \tag{11}$$

where γ_f^p is the filler polar surface energy and γ_p^p is the polymer polar surface energy.

The second modification concerns F, which can be determined experimentally with eq. (10) for each filler instead of being approximated on the basis of the aspect ratio. In the updated Mamunya model, the experimentally determined values for F (shown in Table III) were used for all three fillers.

The third modification involves using the properties of each as-received material, which would reduce the

amount of experimental work needed to use a predictive model. Therefore, the σ_c term (the composite electrical conductivity at the percolation threshold, which is determined experimentally) in eq. (7) was replaced with σ_p (the pure polymer electrical conductivity). The values for σ_c and σ_p are typically very close to each other. The composite conductivity stays at the same order of magnitude as that of the polymer until the filler volume fraction is greater than the percolation threshold.

As a result of all these changes, the parameters A and B had to be recalculated by a linear regression (K vs γ_{pf}) of the experimental results. Specifically, the A value in the equation for K was changed from 0.28 to 0.11, and the value for B was changed from −0.036 to +0.03. The sign of B was changed to reflect the results of the surface energy analysis. The results showed that the polymers would be best matched with fillers of similar surface energy, or that the best combination would have a minimal interfacial tension value (γ_{pf}).[12,13] Therefore, increased dispersion and maximum electrical conductivity would be achieved with a lower interfacial tension. With these new values, the constant n was changed from 0.75 to 0.70 so that the experimental data from all the formulations could be fit.

For the updated (modified) Mamunya model, the following equation was used:

$$\log \sigma = \log \sigma_P + (\log \sigma_F - \log \sigma_P)\left(\frac{\phi - \phi_c}{F - \phi_c}\right)^k$$

$$k = \frac{K\phi_c}{(\phi - \phi_c)^{0.7}}$$

$$K = 0.11 + 0.03\gamma_{pf} \tag{12}$$

In addition, eq. (10) was used to calculate F, and eq. (11) was used to calculate γ_{pf}.

Modeling analysis with the updated Mamunya model

Tables II–IV show the information used as input for these models. Figures 10 and 11 display the electrical conductivity results in comparison with the calculations from both the original and updated (modified) Mamunya models for the carbon-black/nylon 6,6

TABLE IV
Input Values for Mamunya Models

Composite	Original Mamunya			Updated Mamunya	
	Log σ_c (S/cm)	Log σ_F (S/cm)	F	Log σ_F (S/cm)	F
Carbon fiber/nylon 6,6	−15.97	−1.02	0.256	−1.42	0.225
Carbon fiber/PC	−17.14	−1.12	0.256	−1.41	0.225
Synthetic graphite/nylon 6,6	−15.97	−3.45	0.238	−3.39	0.238
Synthetic graphite/PC	−17.14	−2.95	0.238	−3.01	0.238
Carbon black/nylon 6,6	−15.97	2.30	0.190	−0.95	0.060
Carbon black/PC	−17.14	2.32	0.190	−0.92	0.060

composites and the carbon-black/polycarbonate composites, respectively. These figures show that the updated Mamunya model fits the experimental results better than the original model.

Figures 12–15 illustrate the electrical conductivity results in comparison with the calculations from both the original and modified (updated) Mamunya models for both polymers containing synthetic graphite and carbon fiber. Again, the updated equation provides a better fit to the experimental data. Therefore, using the vibrated bulk density to determine F, along with the Owens and Wendt equation for γ_{pf}, resulted in an improved model. The model is highly dependent on the conductivity at F. For this model to work properly, it is necessary to use an accurate F value.

Additive model

The formulation of a new electrical conductivity model will now be discussed. An article by Lux[32] describes four basic electrical conductivity model types: statistical, thermodynamic, geometric, and structure-oriented. In this study, a new type of model is proposed that incorporates various elements from each type. One supposition is the idea of formulating a model based on the rule of mixtures or the general combining rules for predicting properties, such as conductivity. With that as the base equation, terms can then be added or subtracted to account for the various factors that have been found to significantly affect composite electrical conductivity.
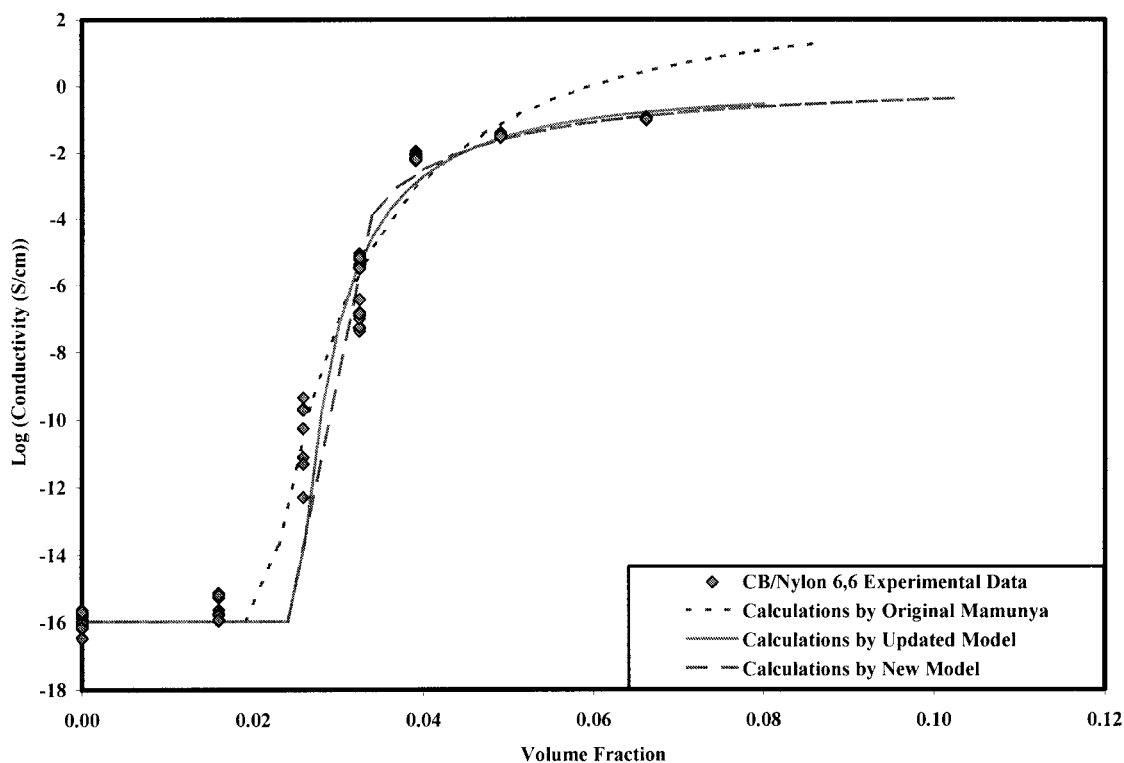

Figure 10 Experimental results compared to original and updated Mamunya models and a new additive model for carbon-black/nylon 6,6 composites.
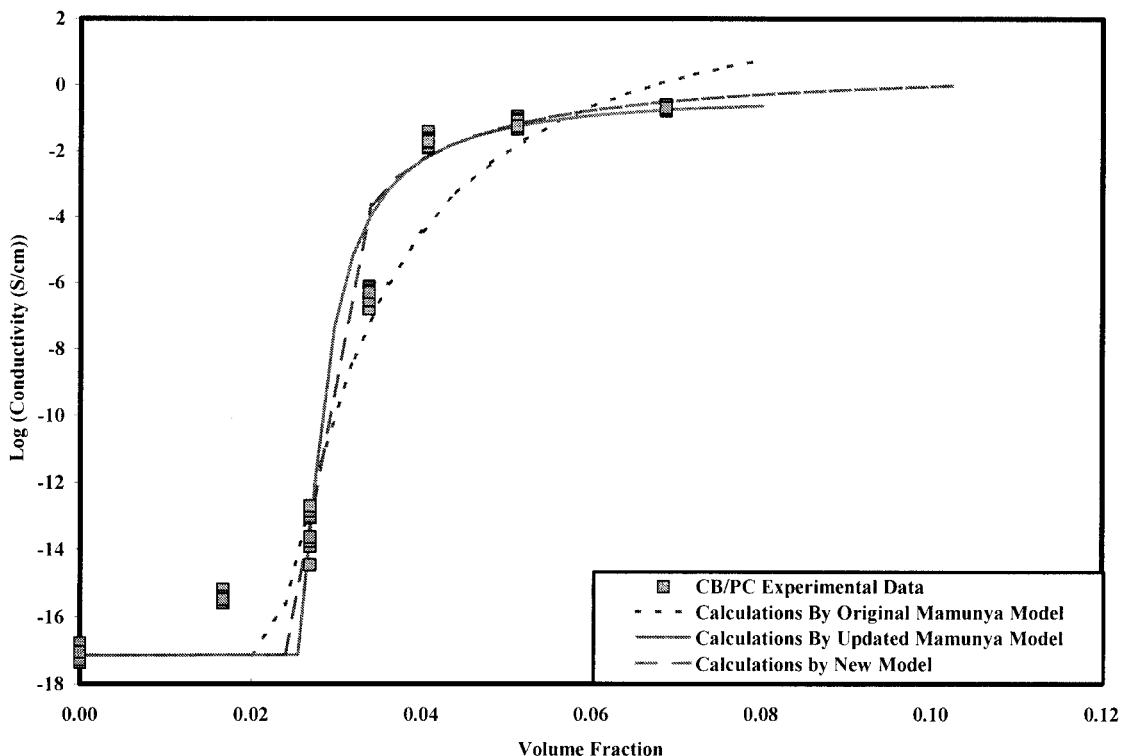
Figure 11 Experimental results compared to original and updated Mamunya models and a new additive model for carbon-black/polycarbonate composites.

McCullough[39] studied the generalized combining rules and their usefulness for predicting several transport properties, including the electrical and thermal conductivity, dielectric constant, and diffusion coefficients. The basic premise was that, although the physical process differed for each of the transport proper-
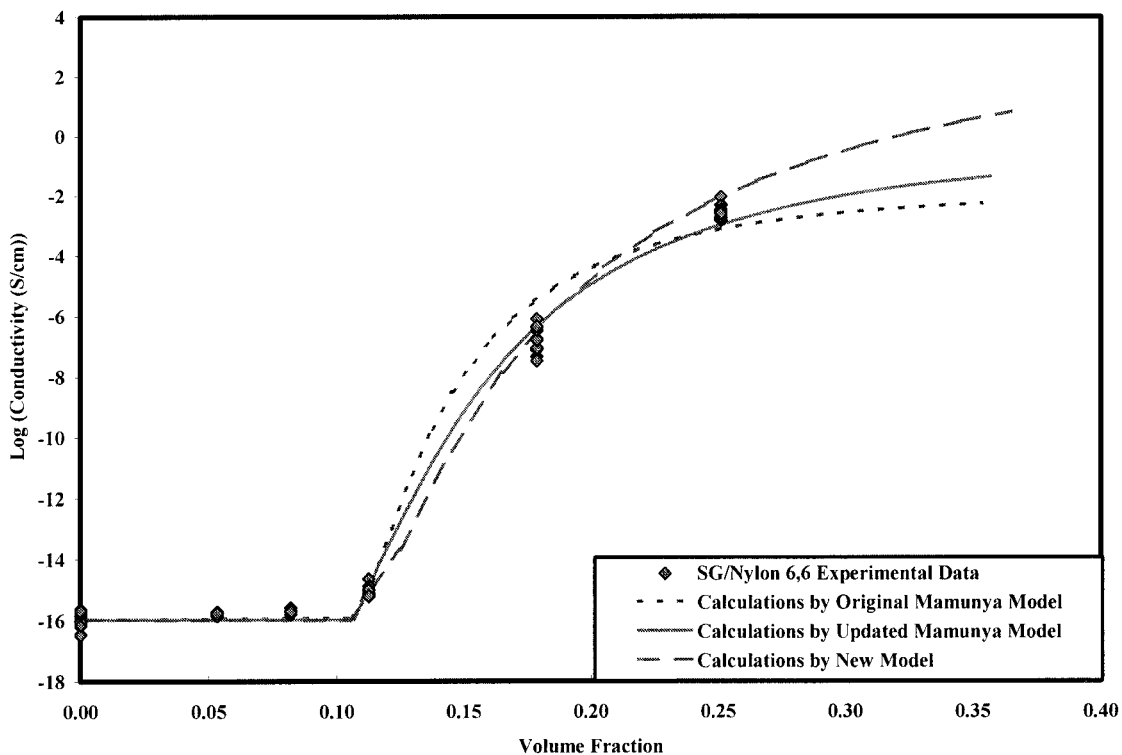

Figure 12 Experimental results compared to original and updated Mamunya models and a new additive model for synthetic-graphite/nylon 6,6 composites.
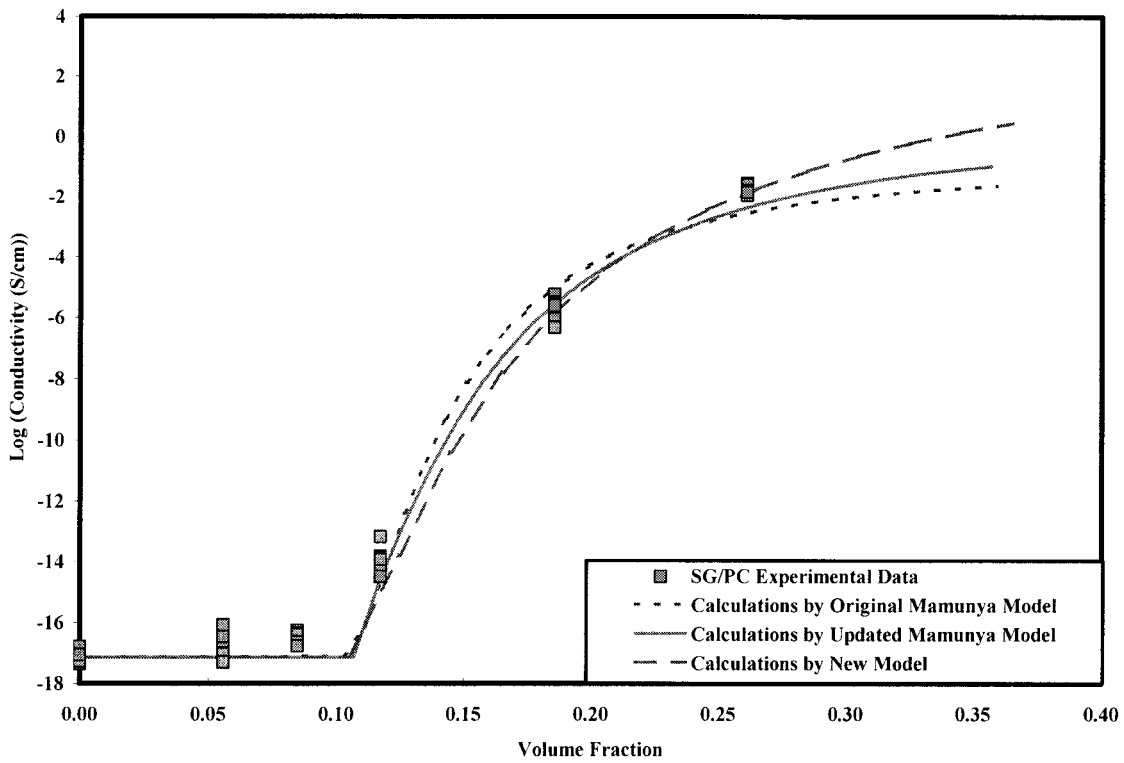
Figure 13 Experimental results compared to original and updated Mamunya models and a new additive model for synthetic-graphite/polycarbonate composites.

ties, the mathematics involved in the constitutive relation suggested that combining rules developed for one set of transport properties could apply to other properties. Then, one general model would be able to predict several different transport properties. The relationship proposed by McCullough as an effective
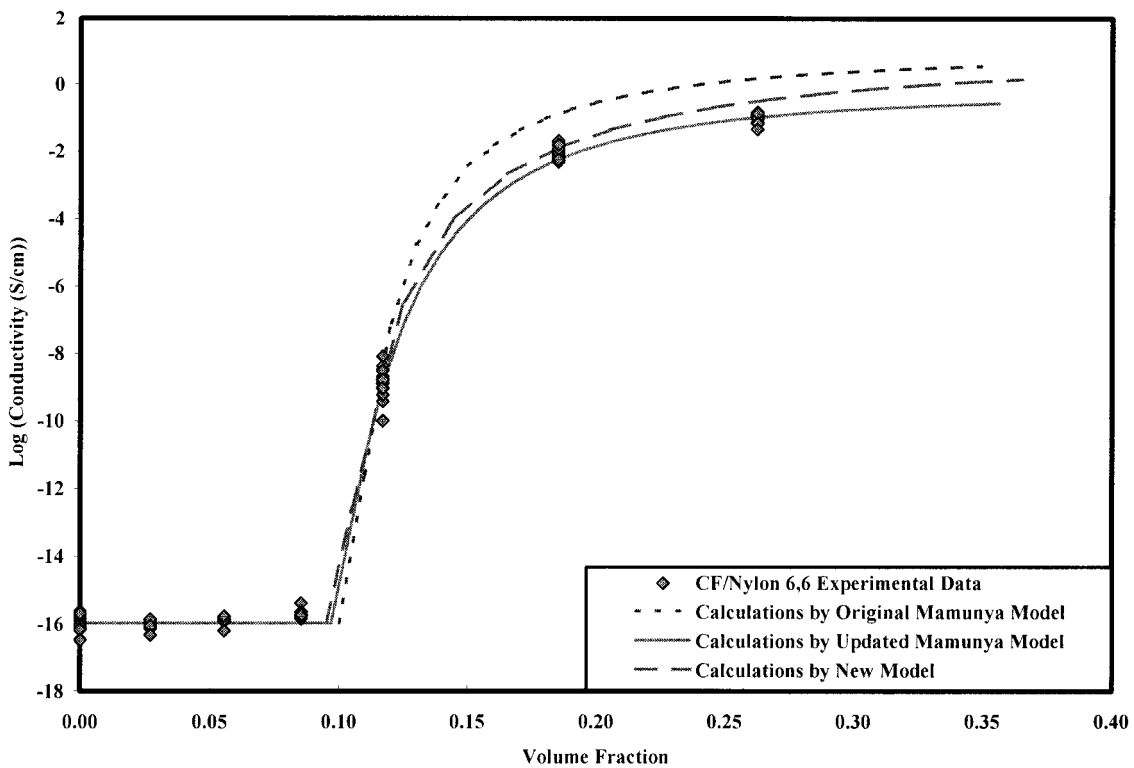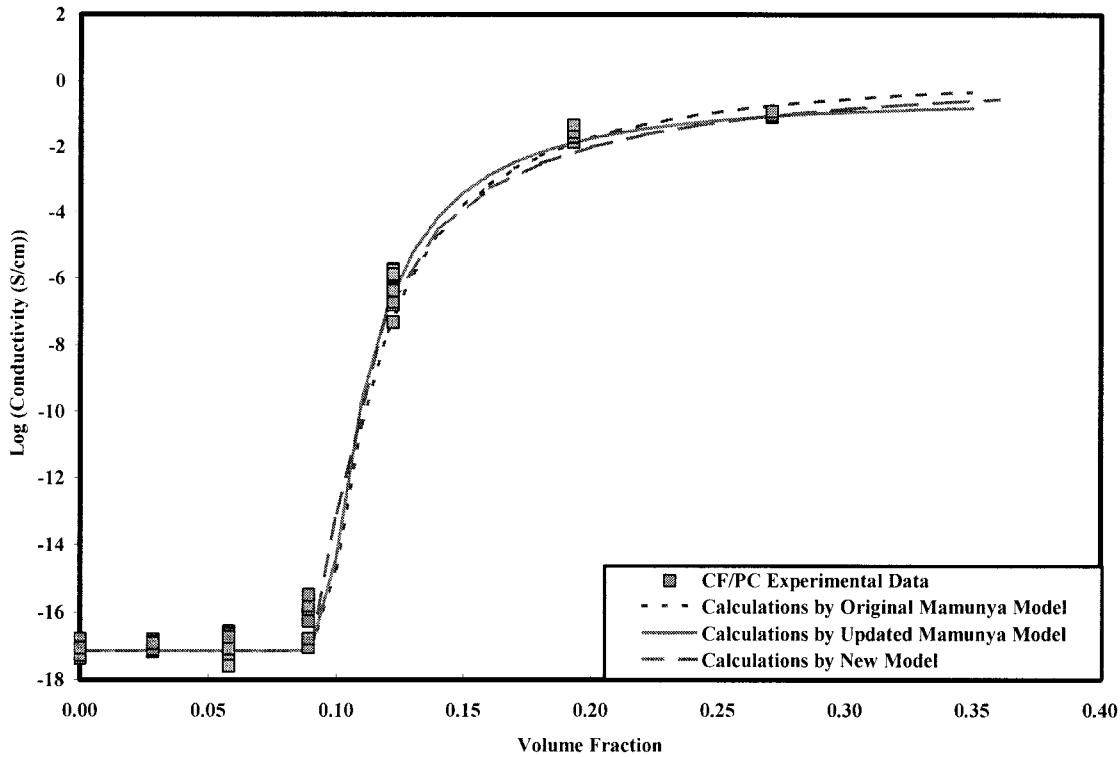

Figure 14 Experimental results compared to original and updated Mamunya models and a new additive model for carbon-fiber/nylon 6,6 composites.

Figure 15 Experimental results compared to original and updated Mamunya models and a new additive model for carbon-fiber/polycarbonate composites.

chain model (e.g., the percolation effect) for transport properties is given in eq. (13):[39]

$$P_i = \phi_f P_f + \phi_m P_m - \left[\frac{\lambda_i \phi_f \phi_m (P_f - P_m)^2}{V_{fi} P_f + V_{mi} P_m} \right] \quad (13)$$

$$V_{fi} = (1 - \lambda_i)\phi_f + \lambda_i \phi_m$$

$$V_{mi} = \lambda_{ie}\phi_f + (1 - \lambda_i)\phi_m$$

$$V_{fi} + V_{mi} = 1$$

The transport property (P) is a general substitution for properties such as the electrical conductivity. This property is a function of the constituent properties, P_f and P_m, the volume fractions, ϕ_f and ϕ_m, and a shape function, λ_i. The subscripts f and m represent the filler and matrix, respectively.

Using this equation, Berger and McCullough[40] were able to fit a set of experimental data for aluminum-filled polyester quite well. Unfortunately, the electrical conductivity results did not follow the typical behavior seen in filled polymers. As much as 45 vol % aluminum had been added to polyester, and there was still no dramatic increase in the conductivity as a results of interparticle contacts. This means that, although this specific equation proposed by McCullough would not work for the filled polymers studied here, a similar basis is behind the idea that is used here for the derivation of a new model. With an equation similar in form to those by McCullough and Mamu-

nya, a new model is proposed, and work is done to fit the model to the experimental data. The new model is a modified mixing rule, in which the various terms account for the constituent conductivity, surface energy, filler volume fraction, aspect ratio, and orientation. Typically, the standard mixing rule, shown in eq. (14), is an inadequate predictor of electrical conductivity for several reasons:

$$\sigma = \sum \phi_i \sigma_i \quad (14)$$

where ϕ_i is the volume fraction of component i and σ_i is the conductivity of component i.

As previously discussed, electrical conductivity results exhibit percolation behavior, by which the conductivity dramatically increases at a characteristic volume fraction. The standard mixing rule does not include this term. However, even if the mixing rule was applied for all volume fractions above the percolation threshold, it would still be a linear relationship, and this is clearly not the trend observed in typical electrical conductivity results. Therefore, it is necessary to use a general combining rule similar to that used by McCullough with the inclusion of a critical exponent that will generate a curve that is representative of electrical conductivity results. The basic form of the equation to be proposed is given in eq. (15):

$$\log \sigma = \begin{cases} \log \sigma_p & \text{for } \phi \leq \phi_c \\ \log \sigma_p + \log \sigma_f \cdot (\phi - \phi_c)^q & \text{for } \phi > \phi_c \\ \quad \pm f(\text{structure}) \pm f(\gamma_{pf}) \end{cases} \quad (15)$$

This equation starts with the base 10 log of the polymer conductivity (σ_p) and then adds or subtracts terms to account for the different factors that affect conductivity, including the structure, interfacial tension (γ_{pf}), filler conductivity (σ_f), filler volume fraction and percolation threshold (ϕ and ϕ_c, respectively), and a critical exponent q. The second term in the equation accounts for the effect of the filler conductivity for all volume fractions above the percolation threshold. This term is very similar to the equation proposed as the original statistical model, as shown in eq. (2).[33] The filler conductivity term is followed by a term to account for the structure of a composite material. This term includes the as-received aspect ratio of the filler particles, as well as a general term to account for the orientation of the filler particles in injection-molded composites. The last term to be added is a function of the interfacial tension, which describes the filler–polymer interaction. In addition to specific values for the factors, such as the aspect ratio and surface energy, it is necessary to include some scaling factors that allow for a more accurate fit of the experimental data.

The first term to be examined is the composite structure term. For the inclusion of the filler aspect ratio and orientation angle, various additional equations that describe the structures of the composites are used. Mamunya used F to incorporate the aspect ratio. In the model studied here, both the aspect ratio and the orientation angle are factors that have been shown to be important. Therefore, an equation is used that describes the shape of the particle based on the aspect ratio, given as the shape factor in eq. (16). The shape factor equation, $h(a)$, is also given in the work by McCullough:[39]

$$h(a) = A^2 \left\{ 1 - \frac{1}{2} \left[A - \frac{1}{A} \right] \times \ln\left[\frac{(A+1)}{(A-1)} \right] \right\} \quad (16)$$

$$A^2 = \frac{a^2}{a^2 - 1}$$

In eq. (16), a is the aspect ratio of the filler, where $1 < a < \infty$. Additionally, the orientation angle for the fillers in the composite must also be included. For the inclusion of this information, the cosine of the angle is used. The results for the orientation angles presented in the previous section all ranged between 0 and 90°. With the cosine of the angle, all values for $\cos(\theta)$ range between 0 and 1 and act as a scaling factor that shifts the conductivity curve according to the alignment of the filler particles. Furthermore, this term is included as an addition because it has been shown that as the aspect ratio increases, the conductivity increases as well. Also, as the orientation angle decreases, the filler is more aligned in the direction of the conductivity measurement. The conductivity should also increase as the cosine of the orientation angle, θ, increases to a

value of 1. Therefore, for this model, the structure term is given as follows:

$$f(\text{structure}) = +h(a) \cdot \cos(\theta) \quad (17)$$

The second term to be examined is the term to account for the interfacial tension, γ_{pf}. Equation (11) is used to determine γ_{pf}. Materials that have similar surface energy values will have a lower interfacial tension. A lower interfacial tension will increase the dispersion of the filler through the matrix. For this reason, and as shown in the updated Mamunya model, the maximum electrical conductivity would be achieved with a lower interfacial tension. For this to be reflected in a model equation, the surface interaction term should increase the conductivity term when the interfacial tension is decreased. Therefore, the surface energy term is given as follows:

$$f(\text{surface energy}) = -C \cdot (\gamma_{pf}) \quad (18)$$

In this equation, C is a constant determined through a curve-fit analysis.

The last portion of the equation to be discussed is the section that accounts for the filler conductivity, σ_f, and the filler volume fraction, ϕ. The parameter of interest in this part of the equation is q. In the original statistical model,[33] which was similar in form to this part of the equation, the critical exponent was a constant value that typically ranged between 1.5 and 3.1. In Mamunya et al.'s equation,[12] the critical exponent k was found to be an inverse function of the volume fraction and percolation threshold of the filler. The value of k was also found to be different for composites with different percolation thresholds. Therefore, the critical exponent for this new model, q, is of the form given in eq. (19), with B and N being constants obtained through regression analysis:

$$q = \frac{B \cdot \phi_c}{(\phi - \phi_c)^N} \quad (19)$$

It is now possible to put the different pieces of the equation together to form a single model for the electrical conductivity. In addition to all of the terms and constants previously discussed, it is also necessary to include another constant, D, which is a scaling factor, to shift the curve into the proper region. The model proposed is given in eq. (20) and is based on the base 10 logarithm of the electrical conductivity of the composite ($\log \sigma$):

$$\log \sigma = \begin{cases} \log \sigma_p & \text{for } \phi \leq \phi_c \\ \log \sigma_p + D \log \sigma_f \cdot (\phi - \phi_c)^{B\phi_c/(\phi - \phi_c)^N} & \text{for } \phi > \phi_c \\ \quad + h(a) \cdot \cos \theta - C\gamma_{pf} \end{cases}$$

$$(20)$$

Composite	Filler log(conductivity) (S/cm)	Polymer log(conductivity) (S/cm)	ϕ_c	Orientation angle (°)	As-received aspect ratio	B	C	D	N
Carbon fiber/nylon 6,6	3.52	−15.97	0.090	25	16.75	0.15	0.15	4.75	0.70
Carbon fiber/PC	3.52	−17.16	0.090	25	16.75	0.15	0.15	4.75	0.70
Synthetic graphite/nylon 6,6	5.00	−15.97	0.105	25	1.8	0.50	0.15	4.00	0.70
Synthetic graphite/PC	5.00	−17.16	0.105	25	1.8	0.50	0.15	4.00	0.70
Carbon black/nylon 6,6	2.00	−15.97	0.025	45	—	0.10	0.15	8.35	0.70
Carbon black/PC	2.00	−17.16	0.025	45	—	0.10	0.15	8.70	0.70

As stated previously, B, C, D, and N are all constants determined through a curve-fit analysis.

Modeling analysis with the additive model

The new additive model presented in eq. (20) is now analyzed with the actual electrical conductivity results. We compared the model curve to experimental data to determine the constants B, C, D, and N and to observe how well an equation of this form fits the experimental data.

The values from Tables I–III were used as inputs for this new model. The orientation angles shown in Table III are means from the in-plane electrical conductivity test ($\phi > \phi_c$). For the carbon-black composites, because no orientation data could be obtained on account of the small size of the carbon black (the primary aggregates were 30–100 nm), it was assumed that the orientation would be random because of the small size and general shape of the particle.[18,41] Therefore, an orientation angle of 45° was used. Additionally, this model also requires the input of an aspect ratio. Because the aspect ratio of a carbon-black particle could not be measured with an optical microscope, a value had to be assumed for this as well. The shape factor equation reaches an upper limit of 1 for very large values of the aspect ratio. Because the carbon-black particles form agglomerates that can then form large chains in a composite,[6,18] a value for the aspect ratio was chosen that was large enough for $h(a)$ to be equal to 1.

Table V also shows the values obtained for the constants B, C, D, and N. The values for C and N, which were 0.15 and 0.70, respectively, were the same for all the materials. Furthermore, the calculated constants B and D were typically the same in both polymers for the carbon fiber and for the synthetic-graphite composites. However, the calculation of common values across all filler materials for the constants was not possible for either B or D, given the significant differences in the filler conductivity and the different percolation threshold values.

The experimental results for the carbon-black-filled composites are compared to the model calculations in Figure 10 for the nylon 6,6-based composites. Figure 11 shows the modeling results for the polycarbonate-based composites. These figures show that the new additive model fits the experimental data better than the original or updated Mamunya model.

Figure 12 shows the experimental results for the synthetic-graphite-filled nylon 6,6-based composites in comparison with the values calculated by the new model. Figure 13 shows the modeling results for the polycarbonate-based composites. These figures show that the experimental data can accurately be modeled by the new additive equation. In fact, in both figures, at each loading level above the percolation threshold, the calculated curve is in the range of the experimental data. Additionally, the curve generated from the new model is comparable to the values calculated by the updated Mamunya model.

Figure 14 shows the experimental results for the carbon-fiber-filled nylon 6,6-based composites in comparison with the values calculated from the new model, and the polycarbonate results are shown in Figure 15. These figures show that the calculations for the new additive model fit the data well for all points above the percolation threshold and are comparable to the updated Mamunya model. The only portion of one curve that did not fall within the range of the experimental data was the 40 wt % (26 vol %) carbon fiber in nylon 6,6. For this point, the experimental data was slightly lower than the calculated values. The difference was approximately one-half of an order of magnitude. Therefore, it is apparent that this type of equation can accurately predict the electrical conductivity of fiber-filled composites.

CONCLUSIONS

From this study, some observations were made regarding electrical conductivity modeling of carbon-filled composites. The updated (modified) Mamunya model fit the experimental results better than the original Mamunya model. Therefore, using the vibrated bulk density to determine F, along with the Owens and Wendt equation for γ_{pf}, resulted in an improved model. A new additive model was proposed that incorporated terms for the constituent electrical conductivities, filler volume fraction, percolation threshold,

filler aspect ratio, filler orientation, and filler–matrix surface energies. This additive model and the updated Mamunya model fit the experimental results well for nylon 6,6-based and polycarbonate-based composites containing carbon black, synthetic graphite, and carbon fiber.

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