

Electrical Conductivity Modeling of Carbon Black/Polycarbonate, Carbon Nanotube/Polycarbonate, and Exfoliated Graphite Nanoplatelet/Polycarbonate Composites

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ABSTRACT: Adding conductive carbon fillers to electrically insulating thermoplastic polymers increases the resulting composite's electrical conductivity, which would enable them to be used in electrostatic dissipative and semiconductive applications. In this study, varying amounts of carbon black (CB: 2 to 10 wt %), multiwalled carbon nanotubes (CNT: 0.5 to 8 wt %), or exfoliated graphite nanoplatelets (GNP: 2 to 15 wt %) were added to polycarbonate (PC) and the resulting composites were tested for electrical conductivity (EC = 1/electrical resistivity). The percolation threshold was ~ 1.2 vol % CNT, ~ 2.4 vol % CB, and ~ 4.6 vol % GNP. In addition, three EC models (Mamunya, additive,

and general effective media) were developed for the CB/PC, CNT/PC, and GNP/PC composites. The general effective media (GEM) model showed the best agreement with the experimental results over the entire range of filler concentrations (above and below the percolation threshold) for all three composite systems. In addition, the GEM model can be easily adapted for composites containing combinations of different conductive fillers. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 182–189, 2012

Key words: carbon nanotubes; carbon black; nanocomposites; polycarbonates

INTRODUCTION

Most polymer resins are electrically insulating. Increasing the electrical conductivity (EC = 1/electrical resistivity, ER) of these resins allows them to be used in other applications, such as electrostatic dissipative (ESD, e.g., handling trays used in electronic equipment assembly, etc., ER typically 10^{10} to 10^3 ohm-cm) and semiconductive (e.g., fuel gauges, etc., ER typically 10^2 to 10^1 ohm-cm) applications. One approach to improving the electrical conductivity of a polymer is through the addition of a conductive filler material, such as carbon and metal.^{1–14} Carbon black (CB) is a relatively inexpensive filler (\sim \$10/lb) that has been used to increase the electrical conductivity (EC) of a resin.^{12,15–18} Recently, carbon nanotubes (CNTs) have been developed and explored for composite electrical conductivity applications.^{19–23} CNTs are still more expensive (\sim \$100/lb) than carbon black. Exfoliated graphite nanoplatelets (xGNPTM) are short stacks of graphene sheets that can be added to polymers to produce electri-

cally conductive composites. Graphite nanoplatelets (GNP) are an alternative to carbon nanotubes since they combine low cost (\sim \$5/lb) and conductivity properties.^{24–28} Polycarbonate is often used for ESD and semiconductive applications.^{18,19,23,28}

A correlation exists between the EC of polymer composites with varying amounts of conductive fillers. At low filler concentrations, the EC is similar to that of the pure polymer. As the filler concentration increases, there is a critical volume fraction (also called the percolation threshold) where the composite EC increases rapidly over a very small range of filler loadings. Further increases in filler content, causes the composite EC to increase slightly until a plateau is observed.²⁹ This relationship has been determined by the thermodynamic model developed by Mamunya et al.,^{30,31} the additive model by Clinger et al.,³² and the General Effective Media (GEM) model by McLachlan et al.^{33–35} All of these EC models are a function of the filler critical volume fraction (percolation threshold) and the filler aspect ratio (length/diameter).

In this work, researchers performed compounding runs followed by injection molding of carbon black/polycarbonate (PC), carbon nanotube/polycarbonate, and graphite nanoplatelet/polycarbonate composites. Composites containing varying amounts of either CB, CNT, or GNP were fabricated and tested

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TABLE I
Properties of Akzo Nobel Ketjenblack EC-600 JD Carbon Black¹⁸

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

for electrical conductivity. The goal of this work was to determine the effects of these fillers on composite electrical conductivity and to apply the Mamunya, additive, and general effective media (GEM) models to these composites. Per the authors' knowledge in the open literature, electrical conductivity models have never been developed for CNT/PC and GNP/PC composite systems.

MATERIALS AND EXPERIMENTAL METHODS

Materials

The matrix used for this project was Sabic's (Pittsfield, MA) Lexan HF1130-111 polycarbonate resin. This polymer has a density of 1.2 g/cm³, a melt flow rate of 25 g/10 min (300°C/1.2 kg), and an electrical resistivity (1/electrical conductivity) of 10¹⁷ ohm-cm.³⁶

The first filler used in this study was Ketjenblack EC-600 JD. This is an electrically conductive carbon black available from Akzo Nobel, Inc. (Chicago, IL). The properties of Ketjenblack EC-600 JD are given in Table I.¹⁸ The carbon black is sold in the form of pellets that are 100 microns to 2 mm in size and, upon mixing into a polymer, easily separates into primary aggregates 30 to 100 nm long.¹⁸

The second filler used was Hyperion Catalysis International's (Cambridge, MA) FIBRILTM nanotubes.¹⁹ This is a conductive, vapor grown, multiwalled carbon nanotube. They are produced from a high purity, low molecular weight hydrocarbons in a proprietary, continuous, gas phase, catalyzed reaction. The outside diameter of the tube is 10 nm and the length is 10 μm, which gives an aspect ratio (length/diameter) of 1000. Due to this high aspect ratio, very low concentrations of nanotubes are needed to produce an electrically conductive composite. This material was provided by Hyperion Catalysis International in a 15 wt % FIBRILTM masterbatch MB6015-00 in PC. Table II shows the properties of the Hyperion Catalysis International FIBRILTM multiwalled carbon nanotube.^{19–21}

The third filler used in this study was exfoliated graphite nanoplatelets that were obtained from

TABLE II
Properties of FIBRILTM Carbon Nanotubes^{19–21}

Composition	Pure carbon
Diameter	0.01 μm
Length	10 μm
Morphology	Graphitic sheets wrapped around a hollow 0.005 μm core
BET (N ₂) surface area	250 m ² /g
Density	2.0 g/cm ³ of nanotube wall 1.75 g/cm ³ for the hollow nanotube

Ovation Polymers as ExtimaTM MB PC1515A, which is a masterbatch of 15 wt % xGnPTM (5 micron average particle diameter and a thickness of 6 to 8 nm, which was manufactured by XG Sciences) in polycarbonate. xGnPTM is a new nanomaterial that can be used to improve the electrical conductivity of a composite.²⁸ The properties of xGnPTM are given in Table III.^{26,28} Photomicrographs of xGnPTM are shown elsewhere.^{26–28}

The concentrations (shown in wt % and the corresponding vol %) for all of the single filler composites tested in this research are shown in Table IV. In this and following tables, figures, and text, the abbreviation "PC" is used to signify polycarbonate, "CB" is used for carbon black, "CNT" is used for carbon nanotubes, and "GNP" is used for exfoliated graphite nanoplatelets. We note that increasing filler amount typically increases composite melt viscosity and, at some point, becomes difficult to extrude and fabricate into a composite part. Thus, a maximum of 10 wt % CB, 8 wt % CNT, and 15 wt % GNP were used. Table IV also shows the electrical resistivity (1/electrical conductivity) results which will be described later in this article.

Test specimen fabrication

Prior to extrusion and injection molding, the Lexan HF1130-111 was dried in an indirect heated dehumidifying drying oven at 121°C for 12 h. Ketjenblack EC-600 JD was used as received. The Hyperion Catalysis International 15 wt % FIBRILTM masterbatch MB6015-00 in PC and the Ovation Polymers ExtimaTM 15 wt % xGNPTM masterbatch MB PC1515A in PC were dried in an indirect heated dehumidifying drying oven at 121°C for 6 h. The extruder used

TABLE III
Properties of Exfoliated Graphite Nanoplatelets^{26,28}

Carbon content	>99.5 wt %
Diameter	5 μm
Thickness	6 to 8 nm
Aspect ratio	~ 700
BET (N ₂) surface area	~ 130 m ² /g
Density	2.0 g/cc

TABLE IV
Single Filler Loading Levels in Polycarbonate and
Electrical Resistivity Results

Formulation	Filler (wt %)	Filler (vol %)	Electrical resistivity (ohm-cm)
PC	0	0.0	$9.37 \times 10^{16} \pm 2.00 \times 10^{16}$ $n = 6$
2CB	2	1.34	$4.05 \times 10^{16} \pm 2.66 \times 10^{16}$ $n = 6$
3CB	3	2.01	$2.85 \times 10^{15} \pm 4.58 \times 10^{14}$ $n = 6$
4CB	4	2.69	$1.17 \times 10^5 \pm 7.77 \times 10^4$ $n = 8$
5CB	5	3.38	2474 ± 646 $n = 8$
6CB	6	4.07	649 ± 18 $n = 8$
8CB	8	5.46	122 ± 4 $n = 8$
10CB	10	6.88	19.5 ± 0.5 $n = 8$
0.5CNT	0.5	0.34	$6.19 \times 10^{16} \pm 1.21 \times 10^{16}$ $n = 6$
1CNT	1	0.69	$2.02 \times 10^{16} \pm 6.62 \times 10^{15}$ $n = 6$
2CNT	2	1.38	4610 ± 1120 $n = 6$
3CNT	3	2.08	216 ± 44 $n = 6$
4CNT	4	2.78	73 ± 10 $n = 6$
5CNT	5	3.48	43 ± 7 $n = 6$
6CNT	6	4.19	18 ± 2 $n = 6$
8CNT	8	5.63	7.8 ± 0.4 $n = 6$
2GNP	2	1.21	$5.46 \times 10^{16} \pm 4.89 \times 10^{15}$ $n = 6$
3GNP	3	1.82	$3.23 \times 10^{16} \pm 7.22 \times 10^{15}$ $n = 8$
4GNP	4	2.44	$1.20 \times 10^{16} \pm 3.54 \times 10^{14}$ $n = 6$
5GNP	5	3.06	$3.76 \times 10^{15} \pm 2.83 \times 10^{14}$ $n = 6$
6GNP	6	3.69	$2.01 \times 10^{14} \pm 4.99 \times 10^{12}$ $n = 6$
8GNP	8	4.96	$3.95 \times 10^7 \pm 1.53 \times 10^7$ $n = 8$
10GNP	10	6.25	$1.74 \times 10^6 \pm 2.65 \times 10^5$ $n = 8$
12GNP	12	7.56	$3.07 \times 10^5 \pm 9.50 \times 10^3$ $n = 5$
15GNP	15	9.57	$2.79 \times 10^4 \pm 8.31 \times 10^3$ $n = 8$

was an American Leistritz Extruder Corp. (Somerville, NJ) Model ZSE 27. This extruder has a 27 mm corotating intermeshing twin screw with 10 zones and a length/diameter ratio of 40. Two different extruder screw designs were used due to the different form of the fillers (CB in a "powder form" and CNT and GNP in PC masterbatch). Both screw designs were chosen to obtain a minimum amount of filler degradation, while still dispersing the filler well in the polymers. The first screw design was used for the CB/PC composites and is shown elsewhere.³⁷ The pure polycarbonate pellets were introduced in Zone 1. Ketjenblack EC-600 JD was introduced in Zone 5. The second screw design was used for the CNT/PC and GNP/PC composites and is shown elsewhere.³⁷ In this case, the pure polycarbonate pellets and the Hyperion FIBRIL™ masterbatch MB6015-00 (containing 15 wt % CNT) or the Ovation Polymers Extima™ 15 wt % xGNP™ masterbatch MB PC1515A in PC were mixed at the appropriate weight ratio to yield the desired CNT or GNP concentration and introduced in Zone 1. The two types of pellets were similar in size; therefore, there was no segregation of pellet type in the feed hopper.

After passing through the extruder, the polymer strands (3 mm in diameter) entered a water bath and then a pelletizer that produced nominally 3 mm long pellets. After extrusion, the polycarbonate based

composites were dried in an indirect heated dehumidifying drying oven at 121°C for 12 h and then stored in moisture barrier bags prior to injection molding.

A Niigata (Tokyo, Japan) injection molding machine, model NE85UA₄, was used to produce test specimens. This machine has a 40 mm diameter single screw with a length/diameter ratio of 18. The lengths of the feed, compression, and metering sections of the single screw are 396 mm, 180 mm, and 144 mm, respectively. A four cavity mold was used to produce 3.3 mm thick ASTM Type I tensile bars (end gated), 3.2 mm thick by 127 mm long by 12.7 mm wide flexural bars (end gated), and 3.4 mm thick with 6.4 cm diameter disks (end gated).

Field emission scanning electron microscope and environmental scanning electron microscope test methods

A JEOL Ltd. JSM-7500F (Tokyo, Japan) field emission scanning electron microscope (FESEM) was used to view the surface of the CB/PC composite (3.2 mm thick by 12.7 mm wide cross section from an injection molded flexural bar). The sample was prepared for observation by mounting the composite in a cast epoxy puck. Then the surface was polished with SiC to a #4000 grit finish, followed by polishing with a 1 micron alumina/water slurry on a rotating lap cloth, and then finally with a 0.05 micron alumina/water slurry in a Buehler Vibromet (Lake Bluff, IL) polisher for 2 h. The composite surface was then etched in O₂ plasma at 23°C and 0.28 Torr for 1 h and then sputter coated with approximately a 10 nm layer of gold. Finally, the samples were observed in the FESEM at 10 kV accelerating voltage, 6 mm working distance using the upper secondary electron detector. This method was used to view the CB in PC.

To view the CNT in the CNT/PC composite, a Hitachi S-4700 (Pleasanton, CA) Cold FESEM was used to view the cryofractured surface of the CNT/PC composite (3.3 mm thick by 12.7 mm wide cross section from an injection molded tensile bar). The samples were prepared for observation by cryo-fracture where the composite was submerged in liquid nitrogen until frozen then quickly retracted and fractured. Afterwards, the samples were attached to aluminum mounting discs and were observed in the FESEM at 2 kV accelerating voltage, 2 mm working distance, using the upper secondary electron detector. This method was used to view the CNT.

A Philips XL40 environmental scanning electron microscope (ESEM) was used to view the surface of the GNP/PC composite (3.2 mm thick by 12.7 mm wide cross section from an injection molded flexural bar). The sample was prepared for observation by mounting the composite in a cast epoxy puck. Then the surface was polished with SiC to a #1200 grit

finish. The sample was then polished using 9 micron diamond suspension and then again with 3 micron diamond suspension on a Buhler Ecomet 4 variable speed grinder-polisher. The surface was finished with a 1 micron alumina/water slurry on the Ecomet 4 and then finally with a 0.05 micron alumina/water slurry in a Buehler Vibromet 1 vibratory polisher for 2 h. The composite surface was then sputter coated with approximately a 10 nm layer of gold by Anatech Ltd. Hummer 6.2 Sputtering System. Finally, the samples were observed in the ESEM at 15 kV accelerating voltage, 15 mm working distance using the upper secondary electron detector.

Electrical resistivity test method

For samples with an electrical resistivity $> 10^6$ ohm-cm, the volumetric electrical conductivity test was conducted. In this method, a constant voltage (100 V) was applied to the as-molded test specimen, and the resistivity was measured according to ASTM D257 using a Keithley 6517A Electrometer/High Resistance Meter (Cleveland, OH) and an 8009 Resistivity Test Fixture.³⁸ The Keithley 6524 High Resistance Measurement Software was used to automate the conductivity measurement. Each test specimen was an injection molded disk that was 6.4 cm in diameter and 3.4 mm thick. Six samples were tested for each formulation. Prior to testing, the samples were conditioned at 23°C and 50% relative humidity for 2 days.

The in-plane volumetric electrical resistivity of the center 60 mm long, 3.3 mm thick, 12.7 mm wide tensile bars (rectangular necked area) injection molded tensile bars was determined according to ASTM D 4496 at 23°C for samples with an electrical resistivity $< 10^6$ ohm-cm.³⁹ Prior to testing, the samples were conditioned at 23°C and 50% relative humidity for 2 days. At least five samples were tested for each formulation. This test was conducted with two probes. In the two probe method, the tensile bar was scratched with a razor blade, placed in liquid nitrogen, and then broken manually at the desired location. Hence, a fracture surface was created on both ends of the in-plane sample. Then the 3.3 mm thick by 12.7 mm wide ends were coated with silver paint and allowed to dry for 1 h. One probe was placed on each silver painted fracture surface and a constant voltage was placed across the sample using a Keithley 2400 Source Meter. The resulting current was also measured on this same Keithley 2400. The volume electrical resistivity is calculated from eq. (1) below:

$$ER = \frac{(\Delta V)(w)(t)}{(i)(L)} \quad (1)$$

where ER = volume electrical resistivity (ohm-cm), ΔV = voltage drop over length of sample (volts), w = sample width (1.27 cm), t = sample thickness

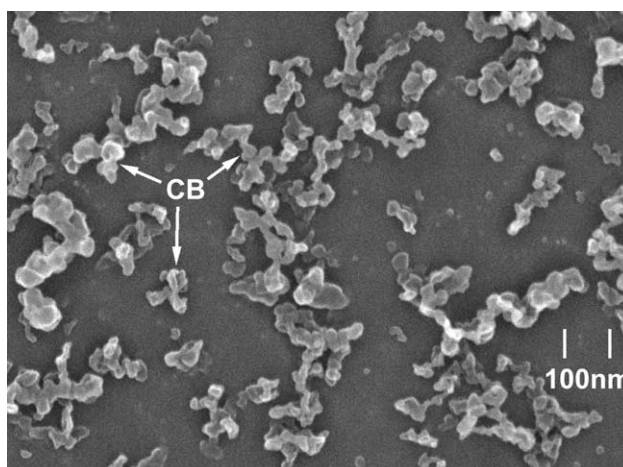


Figure 1 Field emission scanning electron microscope micrograph of 6 wt % CB in polycarbonate.

(0.33 cm), i = current (amps), and L = length over which ΔV is measured (6 cm).

RESULTS

Field emission scanning electron microscope and environmental scanning electron microscope results

Figure 1 shows the CB (white spheres) in the sample containing 6 wt % CB. As expected, a nanosize highly structured carbon black is seen and numerous conductive paths are present due to the close proximity of the carbon black to each other.¹² Figure 2 shows the CNT in sample containing 6 wt % CNT in PC. The high aspect ratio of the CNT is evident in this figure. Figure 3 shows the GNP (white nanoplatelets) in the sample containing 5 wt % GNP in PC.

Electrical resistivity results

The electrical resistivity (ER) results (mean, standard deviation, and number of samples tested) for each

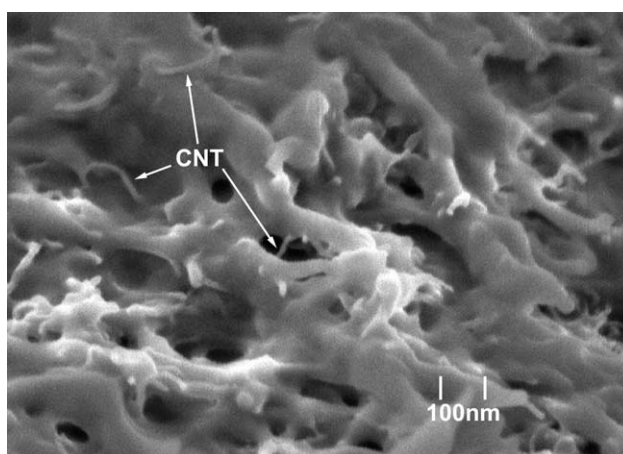


Figure 2 Field emission scanning electron microscope micrograph of 6 wt % CNT in polycarbonate.

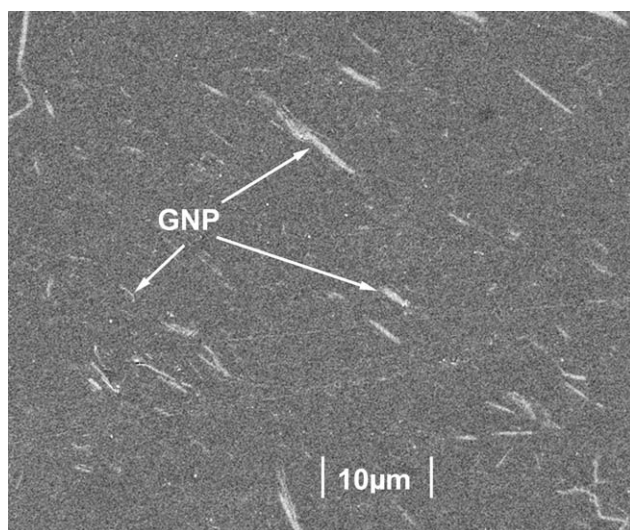


Figure 3 Environmental scanning electron microscope micrograph of 5 wt % GNP in polycarbonate.

formulation containing varying amounts of single fillers are shown in Table IV. Figures 4–6 show the electrical conductivity ($EC = 1/ER$) as a function of filler volume fraction, along with models that will be described later in this article. All the data points have been plotted in these figures. As an example, Figure 4 shows the $\log(\text{electrical conductivity in S/cm})$ for composites containing varying amounts of CB as a function of filler volume fraction. At low filler loadings, the electrical resistivity remains similar to that of the pure polymer. Then, at a point called the percolation threshold the conductivity increases dramatically over a very narrow range of filler concentrations. At higher filler loadings, the electrical resistivity begins to level out again at a value many orders of magnitude above that of the pure polymer.^{5,29}

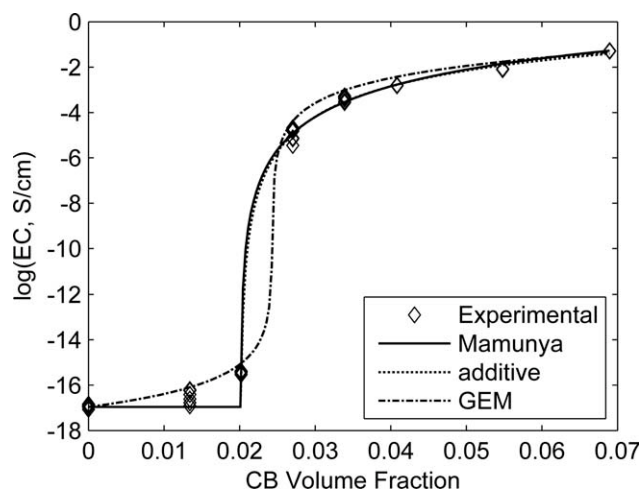


Figure 4 Electrical conductivity results along with Mamunya, additive, and GEM models for CB/PC composites.

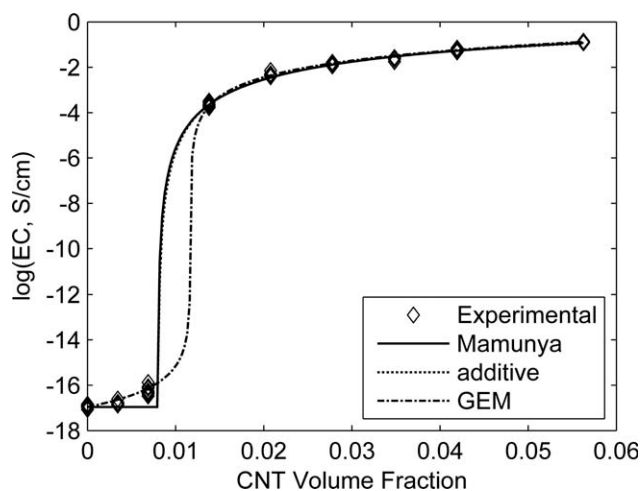


Figure 5 Electrical conductivity results along with Mamunya, additive, and GEM models for CNT/PC composites.

Figure 4 illustrates that carbon black is effective at decreasing the electrical resistivity ($1/\text{electrical conductivity}$) at low filler loadings. The pure polycarbonate has a mean electrical resistivity of 9.4×10^{16} ohm-cm (or 1.07×10^{-17} S/cm), which agrees with the vendor literature value. The percolation threshold occurs at approximately 2.4 vol % (3.6 wt %) for carbon black. At the highest filler concentration, the carbon black produced a mean composite ER of 20 ohm-cm or EC of 0.05 S/cm (10 wt % = 6.9 vol %).

Figure 5 shows the electrical conductivity as a function of volume fraction CNT. The percolation threshold for the CNT/PC composites is ~ 1.2 vol % (1.7 wt %) CNT. At the highest filler concentration, the carbon nanotubes produced a mean composite ER of 7.8 ohm-cm or EC of 0.13 S/cm (8 wt % = 5.6 vol %). The lower percolation threshold for the CNT/PC composites is likely due to the extremely

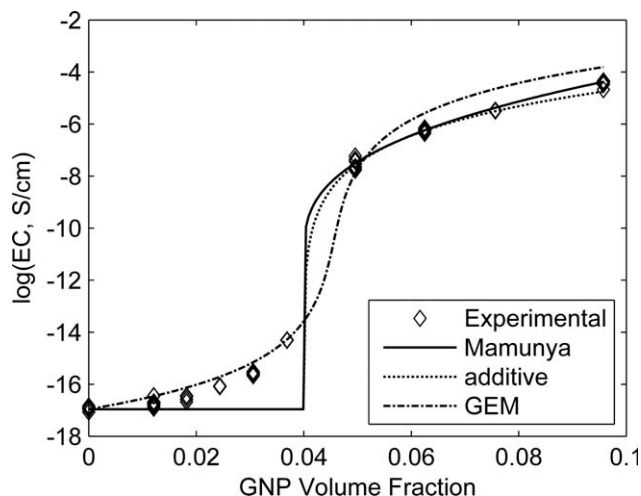


Figure 6 Electrical conductivity results along with Mamunya, additive, and GEM models for GNP/PC.

high aspect ratio (length/diameter) of 1000 for CNT. This same high aspect ratio for CNT also likely increases the electrical conductivity (1/electrical resistivity) as compared to similar concentrations of CB. For example, for 8 wt % (5.6 vol %) CNT, the ER was 7.8 ohm-cm as compared to 122 ohm-cm for 8 wt % (5.5 vol %) CB.

Figure 6 displays the electrical conductivity as a function of volume fraction GNP. For GNP/PC composites, the percolation threshold is higher, at ~ 4.6 vol % (7.4 wt %) GNP. At the highest filler concentration, GNP produced a mean composite ER of 2.8×10^4 ohm-cm or EC of 3.6×10^{-5} S/cm (15 wt % = 9.6 vol % GNP).

Electrical conductivity models

For the electrical modeling portion of the study, our research group focused on the modified version of Mamunya et al.'s thermodynamic model,^{30,31,40} Clingerman et al.'s additive model,^{32,40} and McLachlan et al.'s GEM model.^{33-35,41,42} For all cases, the adjustable model parameters are chosen to minimize the total error, given by:

$$\varepsilon = \sum_{i=1}^n (\log(\sigma_{\text{calc}}) - \log(\sigma_{\text{measured}}))^2 \quad (2)$$

where ε is the total error, σ_{calc} is the electrical conductivity predicted by the model and σ_{measured} is the electrical conductivity found through experimentation. The total error ε is used in this article to compare how well the three models compare with the experimental results for the CB/PC, CNT/PC, and GNP/PC composites. A lower total error ε indicates better model agreement.

The modified Mamunya model predicts the electrical conductivity of a polymer composite using eq. (3) shown below:

$$\log(\sigma) = \log(\sigma_p) + [\log(\sigma_f) - \log(\sigma_p)] \left(\frac{\phi - \phi_c}{F - \phi_c} \right)^k \quad (3)$$

where σ is the composite electrical conductivity (S/cm), σ_p is the electrical conductivity of the polymer (S/cm), ϕ is the filler volume fraction, ϕ_c is the filler volume fraction at the percolation threshold, F is the maximum filler volume fraction, and σ_f is the electrical conductivity of the composite at F (S/cm). The parameter k is given by eq. (4)³¹ defined as:

$$k = \frac{K\phi_c}{(\phi - \phi_c)^n} \quad (4)$$

where K and n are adjustable model parameters.³¹ It should be noted that, for the Mamunya model, when filler volume fractions are less than the

percolation threshold, it is assumed that the composite electrical conductivity is equal to the electrical conductivity of the pure polymer.

For all formulations, $\sigma_p = 1.07 \times 10^{-17}$ S/cm. The Mamunya model fit along with the experimental results for the CB/PC composites are shown in Figure 4, with $\sigma_f = 0.052$ S/cm, $F = 0.069$, $\phi_c = 0.020$, $K = 3.47$ and $n = 0.13$. The total error ε was 2.56 (log S/cm).² The Mamunya model fit along with the experimental results for the CNT/PC composites are shown in Figure 5, with $\sigma_f = 0.128$ S/cm, $F = 0.056$, $\phi_c = 0.008$, $K = 4.11$ and $n = 0.19$. The total error ε was 0.53 (log S/cm).² Figure 6 shows the experimental results along with the Mamunya model fit for the GNP/PC composites, with $\sigma_f = 3.59 \times 10^{-5}$ S/cm, $F = 0.096$, $\phi_c = 0.040$, $K = 6.42$ and $n = -0.099$. The total error ε was 10.1 (log S/cm).² This model shows good agreement for all three composite systems with the bulk of the data. The majority of the error comes from the assumption that the EC below the percolation threshold is the same as the EC of the pure polymer. There is more error for the GNP/PC composites since the EC curve increases more gradually as compared to the CB/PC and CNT/PC composites.

The additive model predicts the electrical conductivity of a polymer composite using eq. (5) shown below:

$$\log(\sigma) = \log(\sigma_p) + H(\phi - \phi_c)^{\frac{G}{(\phi - \phi_c)^n}} + E \quad (5)$$

where σ is the composite electrical conductivity (S/cm), σ_p is the electrical conductivity of the polymer (S/cm), ϕ is the filler volume fraction, and ϕ_c is the filler volume fraction at the percolation threshold. H , G , n , and E are adjustable model parameters.⁴⁰ It should be noted that, similarly to the Mamunya model, the additive model also assumes that the composite EC is equal to the polymer EC below the percolation threshold.

Figures 4, 5, and 6 display the experimental results for the CB/PC composites, CNT/PC composites, and GNP/PC composites, respectively, along with the additive model fits. For the CB/PC system, the following parameters were used: $\phi = 0.020$, $H = 18.3$, $G = 2.72 \times 10^{-2}$, $n = 0.23$, and $E = 0.0$. The total error ε was 2.55 (log S/cm).² For the CNT/PC composites, the following parameters were used: $\phi_c = 0.008$, $H = 17.5$, $G = 1.28 \times 10^{-2}$, $n = 0.28$, and $E = 0.0$. The total error ε was 0.52 (log S/cm).² For the GNP/PC composites, the following parameters were used: $\phi_c = 0.040$, $H = 17.5$, $G = 0.112$, $n = 0.040$, and $E = 0.0$. The total error ε was 9.79 (log S/cm).² The Mamunya and additive models fit the experimental results in a similar manner over the entire range of filler volume fraction for all three composite systems and show good agreement with most of the data.

Again, the majority of the error comes from the assumption that the EC below the percolation threshold is the same as the EC of the pure polymer.

The GEM model predicts the electrical conductivity of a polymer composite using eq. (6) as shown below:

$$\frac{(1 - \phi)(\sigma_l^{1/t} - \sigma_m^{1/t})}{\sigma_l^{1/t} + A\sigma_m^{1/t}} + \frac{\phi(\sigma_h^{1/t} - \sigma_m^{1/t})}{\sigma_h^{1/t} + A\sigma_m^{1/t}} = 0 \quad (6)$$

where σ_m is the composite electrical conductivity (S/cm), σ_l is the electrical conductivity of the polymer (S/cm) and is 1.07×10^{-17} S/cm, σ_h is the electrical conductivity of the filler (S/cm), ϕ is the filler volume fraction, and ϕ_c is the filler volume fraction at the percolation threshold. A is given by eq. (7).

$$A = \frac{1 - \phi_c}{\phi_c} \quad (7)$$

A dimensionless critical component, t , that can be used to determine the morphology of the conducting particles, is given by eq. (8)³⁵ below:

$$t = \frac{1 - \phi_c}{1 - L} \quad (8)$$

where ϕ_c is the filler volume fraction at the percolation threshold and L is the demagnification coefficient of the dispersion.^{33,34} The shape characteristics of the conducting particles in the insulating polymer matrix can be determined from the value of L .

For the GEM model, the EC of the filler, σ_h is needed. For CB, $\sigma_h = 100$ S/cm (see Table I). The EC of single-wall carbon nanotubes has been measured to be $\sim 10^3$ S/cm, which exceeds that of multiwalled carbon nanotubes by an order of magnitude.^{43–45} Thus, in this work for the multiwalled CNT we used $\sigma_h = 100$ S/cm. The EC for GNP has been measured to be between 1 and 100 S/cm.²⁸ In this article, for GNP we used $\sigma_h = 10$ S/cm.

Figures 4, 5, and 6 also display the experimental results for the CB/PC composites, CNT/PC composites, and GNP/PC composites, respectively, along with the GEM model. For the CB/PC composite, the following parameters were used: $t = 2.5$ and $\phi_c = 0.024$, which resulted in a total error ε of 0.55 (log S/cm).² For the CNT/PC composites, the following parameters were used: $t = 2.1$ and $\phi_c = 0.012$, which gave a total error ε of 0.07 (log S/cm).² For the GNP/PC composites, following parameters were used: $t = 3.8$ and $\phi_c = 0.046$, which gave a total error ε of 1.04 (log S/cm).² The value of t has a strong influence on the shape of the model curve. A higher value of t leads to a more gradual change in EC near the percolation. The GEM model shows the best agreement for all three composite systems, especially for the GNP/PC composites. In prior work conducted by our research group, the Mamunya,

additive, and GEM models have been successfully used for CB/polypropylene (PP), and CNT/PP composites.⁴⁶ In addition, the GEM model worked well for CB/Vectra (liquid crystal polymer) composites.⁴¹ To the authors' knowledge, in the open literature, this is the first EC modeling done on CNT/PC and GNP/PC composite systems.

CONCLUSIONS

In this work, the electrical conductivity of CB/PC, CNT/PC, and GNP/PC composites were determined. All of the experimental results exhibit the typical percolation phenomena where at low filler concentrations, the composite has electrical conductivities comparable to the polymer. Above the percolation threshold, the composite has an electrical conductivity up to 16 orders of magnitude higher than that of the polymer. CNT/PC composites display the lowest percolation threshold at ~ 1.2 vol %. CB/PC composites display a slightly higher percolation threshold of ~ 2.4 vol %. GNP/PC composites have a threshold significantly higher at ~ 4.6 vol %.

The Mamunya and additive models show the best agreement with experimental data above the filler percolation threshold. However, the assumption that, below the threshold the composite EC is equal to the EC of the polymer, does not agree with experimental results. The GEM model does not include this assumption and thus, while not having as high of an agreement with the data above the percolation threshold, has a lower total error ε for all three composite systems over the entire range of filler concentrations. It is noted that for the GEM model, the critical volume fraction is near the inflection point in the graph, whereas, for the Mamunya and additive models the critical volume fraction is located where the EC rapidly rises from the baseline polymer value. Some advantages of the GEM model are that it does not rely upon the conductivity of the composite with the highest volume fraction (σ_f at $\phi = F$) and that it can be applied to composite systems that contain more than one type of conductive filler. Therefore, the GEM model agrees with the EC experimental results for CB/PC, CNT/PC, and GNP/PC composites over the entire range of filler concentrations, below and above the percolation threshold, over a range of 16 orders of magnitude. This model could be used for composites for electrostatic dissipative and semiconductive applications. To the authors' knowledge, this is the first EC modeling done on CNT/PC and GNP/PC composites.

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