Tensile Modulus Modeling of Carbon Black/Polycarbonate, Carbon Nanotube/Polycarbonate, and Exfoliated Graphite Nanoplatelet/Polycarbonate Composites

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ABSTRACT: Conductive fillers are often added to thermoplastic polymers to increase the resulting composite's electrical conductivity (EC) which would enable them to be used in electrostatic dissipative and semiconductive applications. The resulting composite also exhibits increased tensile modulus. The filler aspect ratio plays an important role in modeling composite EC, and tensile modulus. It is difficult to measure the filler aspect ratio after the manufacturing process (often extrusion followed by injection molding) in the composite, especially when nanomaterials are used. The EC percolation threshold is a function of the filler aspect ratio; hence, knowledge of this percolation threshold provides a means to extract the filler aspect ratio. In this study, the percolation threshold of the composite was determined from EC measurements and modeling, which in turn was used to determine the filler aspect ratio for tensile modulus modeling. Per the authors' knowledge, this approach has not been previously reported in the open literature. The fillers; carbon black (CB: 2–10 wt %), multiwalled carbon nanotubes (CNT: 0.5–8 wt %), or exfoliated graphite nanoplatelets (GNP: 2–12 wt %); were added to polycarbonate (PC) and the resulting composites were tested for EC and tensile modulus. With the filler aspect ratio determined from EC values for CNT/PC and GNP/PC composites, the three-dimensional randomly oriented fiber Halpin-Tsai model accurately estimates the tensile modulus for the CNT/PC composites and the Nielsen model predicts the tensile modulus well for the CB/PC and GNP/PC composites. J Appl Polym Sci 124: 2269–2277, 2012

Key words: nanocomposites; polycarbonates; tension; carbon black; carbon nanotube

INTRODUCTION

Most polymer resins are electrically insulating. Increasing the electrical conductivity (EC) (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}–10^{3} ohm-cm) and semiconductive (e.g., fuel gauges, etc., ER typically 10^{2}–10^{1} ohm-cm) applications. One approach to improving the EC 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 (~ $ 10/lb) that has been used to increase the EC of a resin.[12,15–18] Recently, carbon nanotubes (CNTs) have been developed and explored for composite EC applications.[19–23] CNTs are still more expensive (~ $ 100/lb) than CB. Exfoliated graphite nanoplatelets (GNP) are short stacks of graphene sheets that can be added to polymers to produce electrically conductive composites. GNP are an alternative to CNTs since they combine low cost (~ $ 5/lb) and good conductivity properties.[24–28]

The electrically conductive composite must also meet application specific tensile modulus values. Adding fillers typically increases the tensile modulus of a composite. The Halpin-Tsai model has been used to model the tensile modulus of composites containing CNT and GNP.[26,29–32] The Nielsen and Halpin-Tsai models have been used to model tensile modulus of CB/nylon 6,6, CB/polypropylene, and CNT/polypropylene composites.[33–37] Both of these models account for constituent properties, concentrations of each constituent, as well as aspect ratio, orientation, and packing of the filler.[29,33–35]

In this work, researchers performed compounding runs followed by injection molding of CB/polycarbonate (PC), carbon nanotube/PC, and graphite nanoplatelet/PC composites. Composites containing

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varying amounts of either CB, CNT, or GNP were fabricated and tested for EC. The first goal of this work was to determine the effects of these fillers on composite EC and tensile modulus. The second goal was to use the EC percolation threshold (point where the composite EC increases rapidly over a small range of filler loadings) to determine the filler aspect ratio in the composite, which is then used to model the composite tensile modulus. Per the authors' knowledge, this approach has not been reported previously in the open literature.

MATERIALS AND EXPERIMENTAL METHODS

Materials

The matrix used for this project was Sabic's (Pittsfield, MA) Lexan HF1130-111 PC resin. This polymer has a density of 1.2 g/cm^3, a melt flow rate of 25 g/10 min (300°C/1.2 kg), and an electrical resistivity (1/EC) of 10^{17} ohm-cm.[38]

The first filler used in this study was Ketjenblack EC-600 JD. This is an electrically conductive CB available from Akzo Nobel (Chicago, IL). The highly branched, high surface area CB structure allows it to contact a large amount of polymer, which results in improved EC at low CB concentrations (often 5 to 7 wt %). The properties of Ketjenblack EC-600 JD are given in Table I.[18] The CB is sold in the form of pellets that are 100 μm to 2 mm in size and, upon mixing into a polymer, easily separates into primary aggregates 30–100 nm long.[18]

The second filler used was Hyperion Catalysis International's (Cambridge, MA) FIBRIL™ nanotubes.[19] This is a conductive, vapor grown, multiwalled carbon nanotube. They are produced from 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. Because of 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 % FIBRIL™ masterbatch MB6015-00 in PC. Table I shows the properties of the Hyperion Catalysis International FIBRIL™ multiwalled CNT.[19–21]

TABLE I
Properties of Fillers[18–21,23,25,28]

Filler properties	Filler values
Ketjenblack EC-600 JD Carbon Black (CB)	
Density	1.8 g/ml
Electrical resistivity	0.01–0.1 ohm cm
BET (N_2) surface area	1250 m^2/g
Fibril™ Carbon Nanotubes (CNT)	
Density	2.0 g/ml nanotube wall; 1.75 g/ml hollow nanotube
BET (N_2) surface area	250 m^2/g
Exfoliated Graphite Nanoplatelets (GNP)	
Density	2.0 g/ml
BET (N_2) surface area	130 m^2/g

TABLE II
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	$3.07 \times 10^{5} \pm 9.50 \times 10^{3}$; $n = 5$

The third filler used in this study was exfoliated GNP that were obtained from Ovation Polymers as Extima™ MB PC1515A, which is a masterbatch of 15 wt % xGnP™ (5 micron average particle diameter and a thickness of 6–8 nm, which was manufactured by XG Sciences) in PC. xGnP™ is a new nanomaterial that can be used to improve the EC of a composite.[28] The properties of xGnP™ are given in Table I.[26,28] Photomicrographs of xGnP™ 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 II. 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 12 wt % GNP were used. Table II also shows the electrical resistivity (1/EC) results that 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 % FIBRIL™ masterbatch MB6015-00 in PC and the Ovation Polymers Extima™ 15 wt % xGNP™ masterbatch MB PC1515A in PC were dried in an indirect heated dehumidifying drying oven at 121°C for 6 h. The extruder used 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.[39] The pure PC 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.[39] In this case, the pure PC 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 PC 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 NE85UA$_4$, 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, 180, and 144 mm, respectively. A four cavity mold was used to produce 3.3 mm thick ASTM Type I tensile bars (end gated) and 3.4 mm thick with 6.4 cm diameter disks (end gated on the bottom edge).

Electrical resistivity test method

For samples with an electrical resistivity $>10^6$ ohm-cm, the volumetric EC test was conducted according to ASTM D257.[40] In this method, a constant voltage (100 V) was applied to the as-molded test specimen, and the resistivity was measured using a Keithley 6517A Electrometer/High Resistance Meter (Cleveland, OH) and an 8009 Resistivity Test Fixture. 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.

For samples with an electrical resistivity $<10^6$ ohm-cm, 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.[41] 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 2 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:

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

where ER is the volume electrical resistivity (ohm-cm), ΔV is the voltage drop over length of sample (volts), w is the sample width (1.27 cm), t is the sample thickness (0.33 cm), i is the current (amps), and L is the length over which ΔV is measured (6 cm).

Tensile test method

The tensile properties (at ambient conditions, 16.5 cm long, 3.3 mm thick ASTM Type I sample geometry) from all formulations were determined using ASTM D638 at a crosshead rate of 5 mm/min for reinforced plastics.[42] An Instru-Met Sintech screw driven mechanical testing machine was used. Tensile modulus was calculated from the initial linear

portion of the stress–strain curve. For each formulation, at least 4 samples were tested. Prior to testing, the samples were conditioned at 23°C and 50% relative humidity for 2 days.

RESULTS

Electrical resistivity results

The ER results (mean, standard deviation, and number of samples tested) for each formulation containing varying amounts of single fillers are shown in Table II. Figures 1–3 show the EC (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 1 shows the log (EC 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.[5,43]

Figure 1 illustrates that CB is effective at decreasing the electrical resistivity (1/EC) at low filler loadings. The pure PC has a mean electrical resistivity of 9.37×10^{16} ohm-cm (or 1.07×10^{-17} S/cm), which agrees with the vendor literature value. The percolation threshold occurs at $\sim$ 2.4 vol % (3.6 wt %) for CB. At the highest filler concentration, the CB produced a mean composite ER of 20 ohm-cm or EC of 0.05 S/cm (10 wt % = 6.9 vol %).

Figure 2 shows the EC as a function of volume fraction of CNT. The 0.5 and 1 wt % CNT in PC composite were only fabricated and tested to determine EC. The percolation threshold for the CNT/PC composites is $\sim$ 1.2 vol % (1.7 wt %) CNT. The lower percolation threshold for the CNT/PC composites is likely due to the extremely high aspect ratio (length/diameter) of 1000 for CNT. This same high aspect ratio for CNT also likely increases the EC (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.

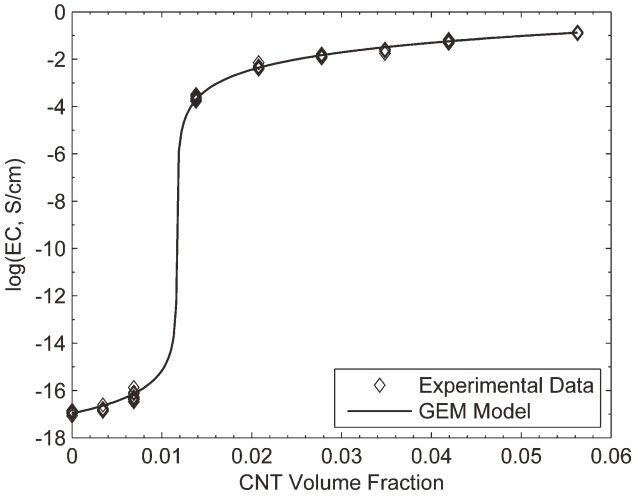

Figure 2 Electrical conductivity results and GEM model for CNT/PC composites.

Figure 3 displays the EC as a function of volume fraction of GNP. For GNP/PC composites, the percolation threshold is higher, at $\sim$ 4.6 vol % (7.4 wt %) GNP. At the highest filler concentration, GNP produced a mean composite ER of 3.1×10^5 ohm-cm or EC of 3.3×10^{-6} S/cm (12 wt % = 7.6 vol % GNP).

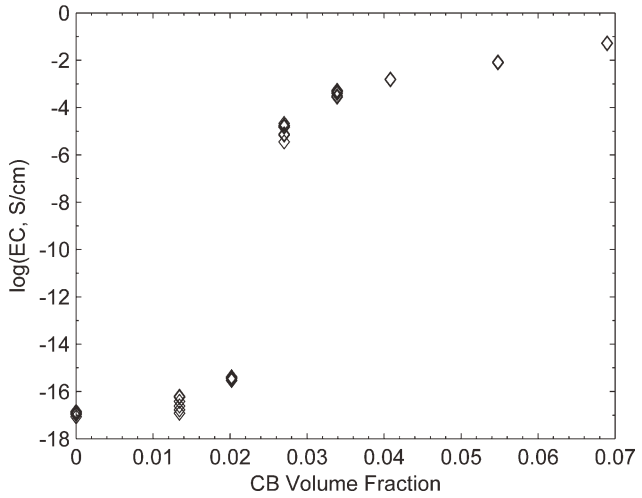

Figure 1 Electrical conductivity results for CB/PC composites.

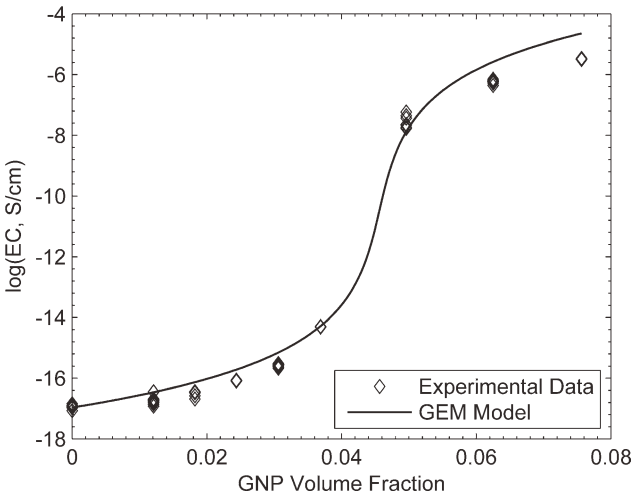

Figure 3 Electrical conductivity results and GEM model for GNP/PC composites.

Electrical conductivity and percolation models

Many models currently used to determine the tensile modulus of filled composites require knowledge of the filler aspect ratio (filler length/diameter if cylindrical). Often filler aspect ratios are only known for the as-received material. When manufacturing composites, the filler aspect ratio in the resulting composite will be lower than as-received values due to the extrusion and injection molding process. Using models for the EC percolation threshold of conductive composites, it is possible to determine an effective filler aspect ratio in the composite. This is especially important for fillers that are very small, such as CNT and GNP. To determine a percolation threshold for these systems, it is necessary to apply EC modeling.

The General Effective Media (GEM) model predicts the EC of a polymer composite using eq. (2) as shown below:

$$\frac{(1-\phi)(\sigma_l^{1/t}-\sigma_m^{1/t})}{\sigma_l^{1/t}+A\sigma_m^{1/t}}+\frac{\phi(\sigma_h^{1/t}-\sigma_m^{1/t})}{\sigma_h^{1/t}+A\sigma_m^{1/t}}=0 \qquad (2)$$

where σ_m is the composite EC (S/cm), σ_l is the EC of the polymer (S/cm) and is 1.07×10^{-17} S/cm, σ_h is the EC of the filler (S/cm), and ϕ is the filler volume fraction. A is given by eq. (3) shown below:

$$A=\frac{1-\phi_c}{\phi_c} \qquad (3)$$

where ϕ_c is the filler volume fraction at the percolation threshold. A dimensionless critical component, t, that can be used to determine the morphology of the conducting particles, is given by eq. (4)[44] below:

$$t=\frac{1-\phi_c}{1-L_D} \qquad (4)$$

where L_D is the demagnification coefficient of the dispersion.[45,46] 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. The EC of single-wall CNTs has been measured to be $\sim 10^3$ S/cm, which exceeds that of multi-walled CNTs by an order of magnitude.[47–49] Thus, in this work for the multi-walled 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 since it provides good agreement with the experimental data. The total error of the model is calculated using eq. (5) below:

$$\varepsilon=\sum_{i=1}^{n}(\log(\sigma_{\text{calc}})-\log(\sigma_{\text{measured}}))^2 \qquad (5)$$

where ε is the total error, σ_{calc} is the EC predicted by the model and σ_{measured} is the EC found through experimentation.

Figures 2 and 3 also display the GEM model results for the CNT/PC composites and GNP/PC composites, respectively. 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] In prior work conducted by our research group, the GEM model has been successfully used for CB/polypropylene (PP), CNT/PP composites, and CB/Vectra (liquid crystal polymer) composites.[50,51]

The percolation threshold for CNT has been recently modeled using an analytical method utilizing an interparticle distance (IPD) concept.[52] This model postulates that there is a certain distance that can physically separate conductive particles without eliminating conduction between the particles. This IPD that still allows conduction is equivalent to the electron tunneling distance through the nonconductive matrix. The model assumes cylindrical morphology for CNT and uses this assumption to determine cubic elements containing a single CNT and then uses these elements to determine a percolation threshold. The resulting analytical formula for the percolation threshold for CNT/PC composites is given by eq. (6)[52] below.

$$\phi_C=\frac{\pi d^2 L}{4[\langle\cos^2\theta\rangle\cdot(L+\text{IPD})]^3} \qquad (6)$$

For this project the percolation threshold from the GEM model will be used to determine an effective length and aspect ratio of the CNT. In eq. (6), ϕ_c is the filler volume fraction at the percolation threshold as found from the GEM model, 0.012; d is the diameter of the CNT, 10 nm; $\langle\cos^2\theta\rangle$ is the average of the squared cosine of the orientation angle of the CNT, for a 3D random distribution this is equal to 1/3; IPD is the electron tunneling distance, 10 nm for many polymer systems[52]; and L is the effective length of the CNT which was then calculated to be 405 nm leading to an effective aspect ratio for CNT of 40.5 for CNT/PC composites.

The percolation threshold for GNP has been recently modeled using a similar analytical method utilizing the IPD concept.[53] This model again postulates that conductive particles can be separated by a distance equal to the electron tunneling distance through the nonconductive matrix and still have conduction between the particles. The model assumes high aspect ratio disc-like morphology for GNP and uses this assumption to determine cubic

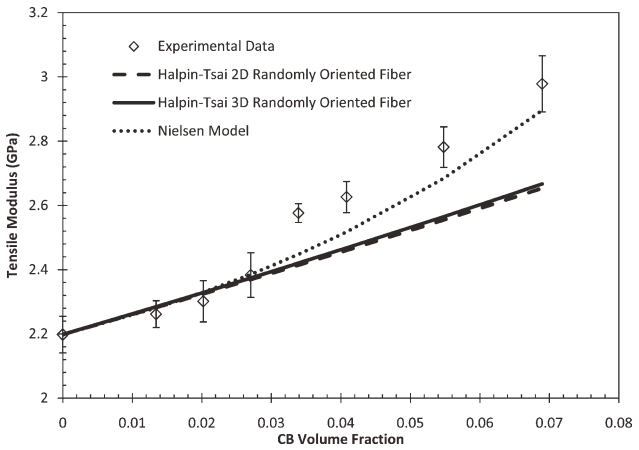

Figure 4 Tensile modulus results along with Halpin-Tsai 2D and 3D randomly oriented fiber and Nielsen Models for CB/PC composites.

elements containing a single GNP and then uses these elements to determine a percolation threshold. The resulting analytical formula for the percolation threshold for GNP/PC composites is given by eq. (7)[53] below.

$$\phi_C = \frac{27\pi D^2 t}{4(D + \mathrm{IPD})^3} \tag{7}$$

For this project, the percolation threshold from the GEM model will be used to determine an effective diameter and aspect ratio (diameter/thickness for a disc) of the GNP. In eq. (7), ϕ_c is the filler volume fraction at the percolation threshold as found from the GEM model, 0.046; t is the thickness of the platelet, 7 nm; IPD is the electron tunneling distance, 10 nm for many polymer systems[53]; and D is the diameter of the platelet which was then calculated to be 3200 nm leading to an effective aspect ratio of 457 for GNP in GNP/PC composites.

Tensile modulus models

Modeling the composite tensile modulus requires knowledge of the filler aspect ratio in the composite being tested. Determining the filler aspect ratio in the resulting composite material can be challenging, especially for small fillers such as CNT and GNP. EC modeling, in conjunction with percolation threshold modeling, provides a method of determining the filler aspect ratio in the composite. To the authors' knowledge, this technique has not been presented previously in the open literature.

Two different tensile modulus models, Halpin-Tsai and Nielsen, will be discussed in this article. The Halpin-Tsai model predicts the tensile modulus of composite materials using the aspect ratio and volume fraction of the filler, as well as the tensile moduli of the matrix and filler. This model shown below does assume that the filler has a cylindrical shape (fiber). Thus, this Halpin-Tsai model is particularly well suited to CNT systems and has often been used to model them.[30–32] The Halpin-Tsai model predicts the composite tensile modulus in both the longitudinal direction and the transverse direction using eqs. (8) and (9) shown below:

$$\frac{E_L}{E_M} = \frac{1 + 2(L/d)\eta_L V_f}{1 - \eta_L V_f} \tag{8}$$

$$\frac{E_T}{E_M} = \frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \tag{9}$$

where E_L is the longitudinal composite tensile modulus, E_T is the transverse composite tensile modulus, E_M is the tensile modulus of the matrix, L/d is the aspect ratio, and V_f is the volume fraction of filler.[29,54–56] The parameters η_L and η_T are given in eqs. (10) and (11) shown below:

$$\eta_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(L/d)} \tag{10}$$

$$\eta_T = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2} \tag{11}$$

where E_f is the tensile modulus of the filler.[29,54–56] Equations (12) and (13) used for models for the two-dimensional (2D) random orientation of fibers and the three-dimensional (3D) random orientation of fibers are shown below:

$$E_C = \frac{3}{8}E_L + \frac{5}{8}E_T \quad \text{2D Randomly oriented fiber} \tag{12}$$

$$E_C = \frac{1}{5}E_L + \frac{4}{5}E_T \quad \text{3D Randomly oriented fiber} \tag{13}$$

where E_C is the composite tensile modulus.[29,54–56]

For all formulations, E_m, the tensile modulus of the matrix was measured experimentally to be 2.20 GPa. Figures 4–6 show the tensile modulus results for the CB/PC, CNT/PC, and GNP/PC systems, respectively. The mean data points are shown along with the error bars (±1 standard deviation). The results for the CB/PC composites are shown in Figure 4, with E_f = 827 GPa and, for a spherical particle, 2(L/d) from eqs. (8) and (10) is replaced with 1.5 as has been done in prior literature.[33,37,57] For the CNT/PC composite, E_f was fit to minimize the error of the Halpin-Tsai 3D randomly oriented fiber model. Error was calculated as the absolute value of the difference between the model value and experimental value for the composite modulus for each formulation. Three-dimensional random orientation was chosen for optimization because of the nature of

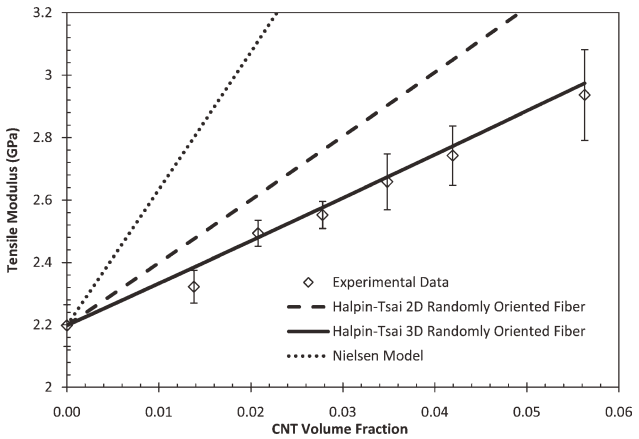

Figure 5 Tensile modulus results along with Halpin-Tsai 2D and 3D randomly oriented fiber and Nielsen models for CNT/PC composites.

the samples since the smallest dimension of the sample (thickness = 3300 μm) was 330 times the length of the as-received CNT (10 μm). Thus, it was determined that E_f = 59.4 GPa, which is similar to the range of values reported by Salvetat et al., 12–50 GPa.[58] The results for the CNT/PC composites are shown in Figure 5 with E_f = 59.4 GPa and L/d = 40.5. The Halpin-Tsai 3D randomly oriented fiber model predicts the tensile modulus of CNT/PC composites well.

To model the GNP/PC system, filler information is needed. Graphene sheets have a tensile modulus of ~ 1000 GPa[28] in the plane of the sheet. GNP is made up of multiple (nominally 10–15) sheets stacked on each other. When tensile loads are transferred to the GNP particles from the polymer, the van der Waals dispersion bonding between layers are likely to fail before graphitic carbon–carbon bonding within the sheets fails, leading to further exfoliation of the particle. Hence, for Halpin-Tsai and Nielsen models, the tensile modulus of GNP was equal to the modulus of exfoliation in the graphite *c*-axis (through-the-plane) of 36.5 GPa.[59] Figure 6 shows the results for the GNP/PC composites with E_f = 36.5 GPa and L/d = 457. The Halpin-Tsai models for the CB/PC (see Fig. 4) and GNP/PC (see Fig. 6) composites do not fit the experimental results well. For both systems, the Halpin-Tsai models consistently underestimate the composite tensile modulus.

The Nielsen model predicts the composite tensile modulus using the tensile modulus and volume fraction of the filler, the tensile modulus of the matrix, the Einstein coefficient of the filler, and the maximum filler packing fraction. The Einstein coefficient, K_E, is related to the filler aspect ratio. For CB, the Einstein parameter is 2.5 for spherical fillers.[60] For CNT, the Einstein parameter is 2 L/d where L/d is the aspect ratio (length/diameter), which leads to a value of 81.[60] For GNP, the Einstein coefficient was determined using eq. (14)[61] below:

$$K_E = 2.5\left(\frac{D}{t}\right)^{0.645} \tag{14}$$

where D is the diameter of the platelet, 3200 nm; t is the thickness of the platelet, 7 nm; and the Einstein coefficient, K_E, was found to be 130. The maximum packing fraction, ϕ_m, is used in the Nielsen model. The maximum packing fraction for CB and CNT have been given in prior work as 0.2.[37] The maximum packing fraction for GNP was found using rheological analysis to be 0.3.[62]

While the Nielsen model does require more inputs than the Halpin-Tsai model, it does not assume a filler geometry. Recall the Halpin-Tsai model discussed here assumes a fiber-shaped filler. Instead, information about the filler geometry is passed into the equation through the Einstein coefficient. This allows the Nielsen model to be better suited to GNP/PC and CB/PC systems than this Halpin-Tsai model since these systems have platelet and spherical geometry fillers, respectively. The Nielsen model uses eqs. (15)–(18) to predict the tensile modulus of composites as shown below:

$$\frac{E_C}{E_m} = \frac{1 + ABV_f}{1 + B\psi V_f} \tag{15}$$

$$A = K_E - 1 \tag{16}$$

$$B = \frac{(E_f/E_m) - 1}{(E_f/E_m) + A} \tag{17}$$

$$\psi = 1 + \frac{1 - \phi_m}{\phi_m^2} V_f \tag{18}$$

where E_C is the composite tensile modulus, E_m is the matrix tensile modulus, E_f is the filler tensile

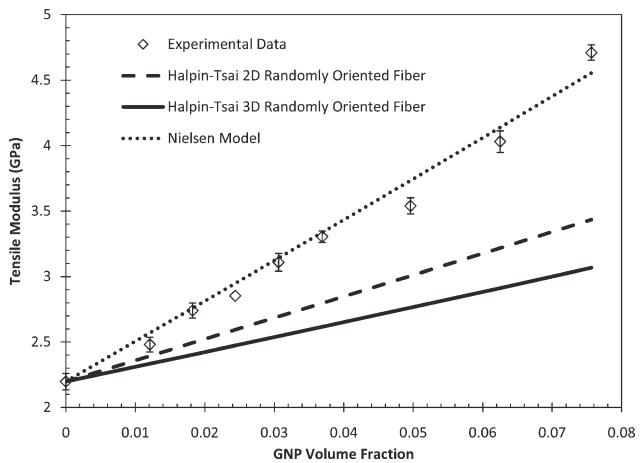

Figure 6 Tensile modulus results along with Halpin-Tsai 2D and 3D randomly oriented fiber and Nielsen models for GNP/PC composites.

modulus, V_f is the filler volume fraction, K_E is the Einstein coefficient, and ϕ_m is the maximum packing fraction of the filler.[33–35,57]

Again, for all formulations, E_m, the tensile modulus of the matrix was 2.20 GPa. The results for the CB/PC composites are shown in Figure 4, with E_f = 827 GPa, K_E = 2.5, ϕ_m = 0.2. The results for the CNT/PC composites are shown in Figure 5, with E_f = 59.4 GPa, K_E = 81.0, ϕ_m = 0.2. Figure 6 shows the results for the GNP/PC composites with E_f = 36.5 GPa, K_E = 130, ϕ_m = 0.3. The Nielsen model shows good agreement for both CB/PC and GNP/PC. The Nielsen model consistently overestimates the tensile modulus of CNT/PC composites.

CONCLUSIONS

In this work, the tensile moduli of CB/PC, CNT/PC, and GNP/PC composites were determined. All of the experimental results exhibit the typical behavior of filled polymers, where the addition of a higher modulus filler increases the composite tensile modulus above that of the matrix. GNP has the greatest effect on increasing the composite tensile modulus. The CNT also causes an increase in modulus, but not as much as GNP. Finally, CB increases the modulus by the smallest amount relative to the other fillers.

The Halpin-Tsai models discussed here assume a fiber-shaped filler and have been often used to model the tensile modulus of composites containing CNTs. For the CNT/PC composites, the 3D randomly oriented fiber Halpin-Tsai model shows very good agreement over the entire range of filler loadings. The Halpin-Tsai models were found to underestimate the composite tensile modulus for CB/PC (spherical filler) and GNP/PC (platelet filler) composites.

The Nielsen model does not assume fiber geometry when modeling composite tensile modulus. The Nielsen model instead depends on the Einstein coefficient of the filler, as well as the maximum packing fraction of the filler. The Einstein coefficient for spherical particles like CB is 2.5. For CNT and GNP, the Einstein coefficients are dependent upon the filler aspect ratio. The filler aspect ratio in the PC composite was found from modeling of the EC percolation threshold. The percolation threshold for CNT/PC and GNP/PC was determined using the GEM model for EC. This approach resulted in improved tensile modulus models. Per the authors' knowledge, this method of determining the aspect ratio of fillers (such as CNT and GNP) in the composite sample via EC percolation threshold values and using this information for tensile modulus modeling, has not been previously reported. The Einstein coefficient for CNT was found to be 81. The Einstein coefficient for GNP was found to be 130. Maximum packing fractions were obtained from prior literature. The Nielsen model shows good agreement with the CB/PC and GNP/PC composites. The Nielsen model overestimates the composite tensile modulus for CNT/PC composites.

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References

1. Taipalus, R.; Harmia, T.; Zhang, M. Q.; Friedrich, K. Compos Sci Tech 2001, 61, 801.
2. Agari, Y.; Uno, T. J. J Appl Polym Sci 1985, 30, 2225.
3. Bigg, D. M. Polym Eng Sci 1977, 17, 842.
4. Bigg, D. M. Adv Polym Technol 1984, 4, 255.
5. Narkis, M.; Lidor, G.; Vaxman, A.; Zuri, L. J Electrost 1999, 47, 201.
6. Nagata, K.; Iwabuki, H.; Nigo, H. Compos Interfaces 1999, 6, 483.
7. Demain, A. Ph.D. Dissertation, Universite Catholique de Louvain, Louvain-la-Neuve, Belgium, 1994.
8. King, J. A.; Tucker, K.W.; Meyers, J. D.; Weber, E. H.; Clingerman, M. L.; Ambrosius, K. R. Polym Compos 2001, 22, 142.
9. Murthy, M. V. In Proceedings of the Society of Plastics Engineers Annual Technical Conference 1396; San Francisco, CA (1994).
10. Simon, R. M. Polym News 1985, 11, 102.
11. Mapleston, P. Mod Plast 1992, 69, 80.
12. Donnet, J. B.; Bansal, R. C.; Wang, M. J. Carbon Black, 2nd ed.; Marcel Dekker: New York, 1993.
13. Huang, J. C. Adv Polym Technol 2002, 21, 299.
14. Bigg, D. M. Polym Compos 1987, 8, 1.
15. Zhou, Z.; Wang, S.; Zhang, Y.; Zhang, Y. J Appl Polym Sci 2006, 102, 4823.
16. Zhang, Q. H.; Chen, D. J. J Mater Sci 2004, 39, 1751.
17. Feng, J.; Li, J.; Chan, C. M. J Appl Polym Sci 2002, 85, 358.
18. Akzo Nobel. Electrically Conductive Ketjenblack Product Literature; 300. S. Riverside Plaza, Chicago, IL, 1999.
19. Hyperion Catalysis International. Hyperion Catalysis International Fibril Product Literature; Hyperion Catalysis International: Cambridge, MA, 2008.
20. Shaffer, M. S. P.; Windle, A. H. Adv Mater 1999, 11, 937.
21. Potschke, P.; Bhattacharyya, A. R.; Janke, A.; Goering, H. Compos Interfaces 2003, 10, 389.
22. Lee, S. H.; Kim, J. H.; Choi, S. H.; Kim, S. Y.; Kim, K. W.; Youn, J. R. Polym Int 2008, 58, 354.
23. Potschke, P.; Abdel-Goad, M.; Pegel, S.; Jehnichen, D.; Mark, J. E. Zhou, D.; Heinrich, G. J Macromol Sci 2010, 47, 12.
24. Kalaitzidou, K.; Fukushima, H.; Drzal, L. T. Compos A: Appl Sci Manufact 2007, 38, 1675.
25. Fukushima, H.; Drzal, L. T.; Rook, B. P.; Rich, M. J. J Therm Anal Calorim 2006, 85, 235.
26. Kalaitzidou, K.; Fukushima, H.; Miyagawa, H.; Drzal, L. T. Polymer Engineering and Science 2007, 47, 1796.
27. Kalaitzidou, K.; Fukushima, H.; Drzal, L. T. Compos Sci Technol 2007, 67, 2045.
28. XG Sciences Inc. xGnP™ Brand Graphene Nanoplatelets Product Information; XG Sciences Inc.: East Lansing, MI, 2010.

29. Halpin, J. C.; Kardos, J. L. Polym Eng Sci 1976, 16, 344.
30. Thostenson, E. T.; Chou, T. W. J Phys D: Appl Phys 2003, 36, 573.
31. Gojny, F. H.; Wichmann, M. H. G.; Kopke, U.; Fiedler, B.; Schulte, K.; Compos Sci Technol 2004, 64, 2363.
32. Peeterbroeck, S.; Breugelmans, L.; Alandre, M.; Nagy, J. B.; Viville, P.; Lazzaroni, R.; Dubois, P. Compos Sci Technol 2007, 67, 1659.
33. Nielsen, L. E. Ind Eng Chem Fundam 1974, 13, 17.
34. Nielsen, L. E.; Landel, R. F. Mechanical Properties of Polymers and Composites, 2nd ed.; Marcel Dekker: New York, 1994.
35. Nielsen, L. E. J Appl Phys 1970, 41, 4626.
36. Konell, J. P.; King, J. A.; Miskioglu, I. J Appl Polym Sci 2003, 90, 1716.
37. Gaxiola, D. L.; Jubinski, M. M.; Keith, J. M.; King, J. A.; Miskioglu, I. J Appl Polym Sci 2010, 118, 1620.
38. One Plastics Avenue. Sabic Innovative Plastics PC Resin Product Brochure, Sabic-PLA-650; One Plastics Avenue: Pittsfield, MA, 2008.
39. Via, M. D.; Morrison, F. A.; King, J. A.; Caspary, J. A.; Mills, O. P.; Bogucki, G. R. J Appl Polym Sci 2011, 121, 1040.
40. American Society for Testing and Materials. Standard Test Methods for DC Resistance or Conductance of Insulating Materials, ASTM Standard D257–91; American Society for Testing and Materials: Philadelphia, PA, 1998.
41. "Standard Test Methods for DC Resistance or Conductance of Moderately Conductive Materials", ASTM Standard D4496–04, American Society for Testing and Materials, Philadelphia, P. A.; (2008).
42. "Standard Test Method for Tensile Properties of Plastics", ASTM Standard D638, American Society for Testing and Materials, Philadelphia, P. A.; (2008).
43. Weber, M.; Kamal, M. R. Polym Compos 1997, 18, 711.
44. McLachlan, D. S. Solid State Commun 1986, 60, 821.
45. McLachlan, D. S.; Newman, R. E. J Am Ceram Soc 1990, 73, 2187.
46. McLachlan, D. S. J Phys C: Solid State Phys 1985, 18, 1891.
47. Dai, H.; Wong, E. W.; Lieber, C. M. Science 1996, 272, 523.
48. Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Lee, Y. H.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tamanek, D.; Fisher, J. E.; Smalley, R. E. Science 1996, 273, 483.
49. Grunlan, J. C.; Liu, L.; Kim, Y. S. Nano Lett 2006, 6, 911.
50. Keith, J. M.; King, J. A.; Johnson, B. A. J New Mater Electrochem Syst 2008, 11, 253.
51. Barton, R. L.; Keith, J. M.; King, J. A. J New Mater Electrochem Syst 2007, 10, 225.
52. Li, J.; Ma, P. C.; Chow, W. S.; To, C. K.; Tang, B. Z.; Kim, J. K. Adv Funct Mater 2007, 17, 3207.
53. Li, J.; Kim, J. K. Compos Sci Technol 2007, 67, 2114.
54. Agarwal, B. D.; Broutman, L. J. Analysis and Performance of Fiber Composites; Wiley: New York; 1980.
55. Mallick, P. K.; Composites Engineering Handbook; Marcel Dekker: New York, 1997.
56. Halpin, J. C. J Compos Mater 1969, 3, 732.
57. Bigg, D. M. Polym Compos 1986, 7, 125.
58. Salvetat, J. P.; Kulik, A. J.; Bonard, J. M.; Briggs, G. A. D.; Stockli, T.; Metenier, K.; Bonnamy, S.; Beguin, F.; Bunham, N. A.; Forro, L.; Nature 1999, 11, 161.
59. Marsh, H.; Rodriguez-Reinoso, F. Sciences of Carbon Materials; Universidad de Alicante: Alicante, Spain, 2001.
60. Nielsen, L. E. Polymer Rheology; Marcel Dekker: New York, 1977.
61. Rao, Y. Q.; Pochan, J. M. Macromolecules 2007, 40, 290.
62. King, J. A.; Via, M. D.; Morrison, F. A.; Wiese, K. R.; Beach, E. A.; Cieslinski, M. J.; Bogucki, G. R. J Compos Mater, in press.