Tensile Modulus Modeling of Carbon-Filled Nylon 6,6 and Polycarbonate-Based Resins

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ABSTRACT: Electrically and thermally conductive resins can be produced by adding conductive fillers to insulating polymers. Mechanical properties, such as tensile modulus, are also important. This research focused on performing compounding runs followed by injection molding and tensile testing of carbon-filled nylon 6,6 and polycarbonate-based resins. The three carbon fillers investigated included an electrically conductive carbon black, synthetic graphite particles, and a milled pitch–based carbon fiber. For each polymer, resins were produced and tested that contained varying amounts of these single-carbon fillers. In addition, combinations of fillers were investigated by conducting a full 2^3 factorial design and a complete replicate in each polymer. These tensile modulus experimental results were then compared to results predicted by several different models. For the composites containing only one filler type, the Nielsen model with the modified Ψ term provided the best prediction of the actual experimental values. For the composites containing more than one filler type, a new parameter, which includes the vibrated bulk density (VBD) of the fillers, was incorporated into the Nielsen model with the modified Ψ term. This model with the new VBD parameter provided the best estimate of experimental tensile modulus for composites containing multiple-filler types. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1716–1728, 2003

Key words: modeling; stiffness; fillers; nylon; polycarbonates

INTRODUCTION

The electrical and thermal conductivity of resins can be increased by the addition of conductive fillers, such as carbon black, synthetic graphite, and carbon fibers.[1–8] The advantages of conductive resins compared to metals (typically used) includes improved corrosion resistance, lighter weight, and the ability to adapt the conductivity properties to suit the application needs. For example, a thermally conductive resin is ideally suited for heat sink applications, such as lighting ballasts and transformer housings. An electrically conductive resin is used in static dissipative, semiconducting (e.g., fuel gages, etc.), or EMI (electromagnetic interference)/RFI (radio frequency interference) shielding applications (e.g., computer and cellular phone housings, etc.).

A significant amount of work has been conducted varying the amount of single conductive fillers in a composite material.[1,4–10] Taipalus et al.[11] studied the electrical conductivity of carbon fiber–reinforced polypropylene/polyaniline complex blends. Limited work has been conducted concerning the effect of combinations of various types of conductive fillers, such as carbon black, synthetic graphite, and carbon fiber on the composite conductivity. Thongruang et al.[12] investigated the electrical conductivity and mechanical properties of composites containing both graphite and carbon fiber in high-density polyethylene and ultrahigh molecular weight polyethylene. Other researchers have studied the synergistic effects of different carbon fillers in nylon 6,6 and polycarbonate on electrical and thermal conductivity.[13,14] However, mechanical properties, such as tensile modulus, are also important and cannot be ignored.

In this research, the authors performed compounding runs followed by injection molding and tensile 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 varying amounts of these single-carbon fillers. In addition, combinations of fillers were investigated by conducting a full 2^3 factorial design and a complete replicate in each polymer. The goal of this study was to compare the experimental results with those predicted by existing tensile modulus models and, if needed, to develop an improved tensile modulus model for short-fiber/particulate composites.

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TABLE I
Filler Loadings in Factorial Design Formulations for Nylon 6,6 and Polycarbonate

Formulation	Ketjenblack EC-600 JD (wt %)	Thermocarb™ TC-300 Specialty Graphite (wt %)	ThermalGraph DKD X (wt %)
No filler	0	0	0
CB	5	0	0
SG	0	30	0
CB + SG	5	30	0
CF	0	0	20
CB + CF	5	0	20
SG + CF	0	30	20
CB + SG + CF	5	30	20

EXPERIMENTAL

Materials

Two matrix materials were used in this project. The first matrix used was DuPont Zytel 101 NC010 (DuPont, Wilmington, DE), an unmodified semicrystalline nylon 6,6. The second matrix used was Lexan HF 1110-111N, which is an amorphous engineering thermoplastic produced by GE Plastics (Pittsfield, MA). The properties of these polymers are discussed elsewhere.[13,15,16]

Three different carbon fillers were used in this project. Akzo (Chicago, IL) Nobel Ketjenblack EC-600 JD, an electrically conductive carbon black, was used. The carbon black structure is highly branched, which results in significantly improved electrical conductivity in a composite. Also, carbon black has a large surface area and thus can contact a large amount of polymer.[17] Thermocarb TC-300 Specialty Graphite, a high-quality synthetic graphite that is available from Conoco Inc. (Houston, TX), was used because of its high thermal and electrical conductivity.[18] BP/Amoco's (Alpharetta, GA) pitch-based milled (200 μm long) carbon fiber, ThermalGraph DKD X, was used to improve the electrical and thermal conductivity and the tensile strength of the resin.[19] The properties of these fillers are described elsewhere.[13,17–19]

In this current study, a 2^3 factorial design (three factors or fillers in this case at two different loading levels) was completed in each polymer. In addition, a complete replicate of the factorial design was also completed in each polymer. For all fillers, the low loading level was 0 wt %. The high loading level varied for each filler. The high levels were 5 wt % for Ketjenblack EC-600 JD, 30 wt % for Thermocarb TC-300 Specialty Graphite, and 20 wt % for ThermalGraph DKD X. Table I shows the factorial design formulations. In Table I, "CB" signifies carbon black, "SG" signifies synthetic graphite for Thermocarb TC-300 Specialty Graphite, and "CF" signifies carbon fiber. Because this project focused on producing highly conductive composites, the high loading levels were chosen so that the filler amounts would be above the electrical conductivity percolation threshold. Another consideration was that the total wt % filler for the composite with all fillers at the high level be 55 wt %. Higher filler amounts would likely make it difficult to extrude and injection-mold the conductive resin into test specimens.

Tensile properties were also measured on composites containing only one type of carbon filler in both nylon 6,6 and polycarbonate. The loading levels for these single-filler composites are shown in Table II.

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 stored in moisture-barrier bags.

The extruder used was an American Leistritz Extruder Corp. Model ZSE 27. This extruder has a 27-mm corotating intermeshing twin screw with 10 zones and a length/diameter ratio of 40. The screw design was chosen to minimize filler degradation, while still dispersing the fillers well 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.

TABLE II
Single Filler Loading Levels for Nylon 6,6 and Polycarbonate

Filler	Loading levels (wt %)
Kejenblack EC-600 JD	2.5, 4.0, 5.0, 6.0, 7.5, 10.0
Thermocarb™ TC-300 Specialty Graphite	10.0, 15.0, 20.0, 30.0, 40.0
ThermalGraph DKD X	5.0, 10.0, 15.0, 20.0, 30.0, 40.0

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 compounding, the pelletized composite resin was dried and then stored in moisture-barrier bags before injection molding.

A Niigata 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 3.2-mm-thick ASTM Type I tensile bars (end-gated). The tensile properties of all formulations were determined.

Tensile test method

The tensile properties (at ambient conditions, 16.5 cm long, 3.2-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.[20] 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. The nylon 6,6–based samples were all tested dry as molded (DAM). The polycarbonate-based samples were conditioned at 50% relative humidity (RH) for 24 h at 23°C before testing. For each formulation, at least five samples were tested.

Filler length and aspect ratio test method

To determine the length of the carbon fiber and synthetic graphite in the tensile test specimens, solvent digestion was used. A 0.2-g sample cut from the center gauge section of a tensile test specimen was dissolved at 23°C using formic acid to remove the nylon 6,6 and methylene chloride to remove the polycarbonate. The fillers were then dispersed onto a glass slide and viewed using an Olympus SZH10 optical microscope with an Optronics Engineering LX-750 video camera. The images (at ×60 magnification) were collected using Scion Image version 1.62 software. The images were then processed using Adobe Photoshop 5.0 and the Image Processing Tool Kit version 3.0. The length and aspect ratio (length/diameter) of each filler was measured. For each formulation, between 300 and 1100 particles/fibers were measured. Because of the extremely small size of the carbon black (primary aggregates are 30 to 100 nm), the length and aspect ratio of the carbon black was not measured.

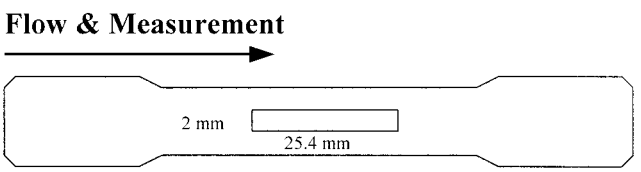

Figure 1 Portion of tensile bar from which orientation specimens were cut.

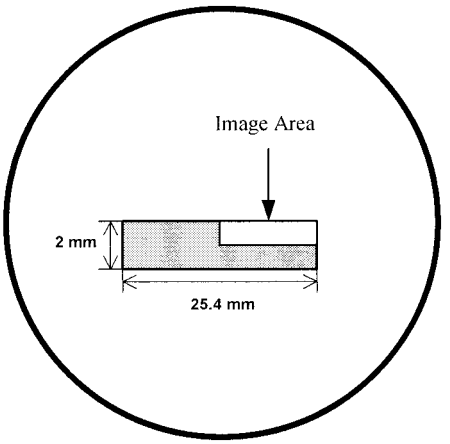

Figure 2 Sample arrangement for filler orientation analysis.

Filler orientation test method

To determine the orientation of the carbon fillers, a polished composite sample was viewed using an optical microscope. Again, because of the small size of the carbon black, the orientations of only the synthetic graphite particles and carbon fibers were determined. One 25 × 2-mm rectangle was cut from the center of a tensile specimen, as shown in Figure 1. This sample was cast in a two-part epoxy plug, as shown in Figure 2. The sample was then polished and viewed using an Olympus BX60 reflected-light microscope at a magnification of ×200. Again, the images were collected using Scion Image version 1.62 software. The images were then processed using Adobe Photoshop 5.0 and the Image Processing Tool Kit version 3.0. For each formulation, the orientation was determined by viewing 700 to 1600 particles/fibers.

Vibrated bulk density test method

The vibrated bulk density (VBD) was determined for each of the three fillers, as well as for combinations of the fillers, by following the general procedure outlined in ASTM D4292-92.[21] The VBD was measured by placing 20 cm^3 of the filler into a 25-cm^3 graduated cylinder. The cylinder was then vibrated at 50 Hz for 5 min at an amplitude of 0.2 mm. The volume was read from the cylinder, and then the VBD was calculated (weight of filler that corresponded to 20 cm^3/vibrated volume of filler). For each filler and combination of fillers, two values were determined.

TENSILE MODULUS MODELS

Many models are used to predict the tensile modulus of a composite.[22] The most basic models are shown below for a three-component system (e.g., 1 matrix material and 2 different fillers).

Rule of mixtures

$$E_c = V_1E_1 + V_2E_2 + V_3E_3 \tag{1}$$

Inverse rule of mixtures

$$\frac{1}{E_c} = \frac{V_1}{E_1} + \frac{V_2}{E_2} + \frac{V_3}{E_3} \tag{2}$$

where, for eqs. (1) and (2), E_c is the composite tensile modulus, V_1 is the volume fraction of component 1, V_2 is the volume fraction of component 2, V_3 is the volume fraction of component 3, E_1 is the tensile modulus of component 1, E_2 is the tensile modulus of component 2, and E_3 is the tensile modulus of component 3.

The rule of mixtures model, sometimes called the series model , is the weighted average of matrix and tensile modulus fillers. This model works well to predict the modulus of a unidirectional composite with continuous fibers but typically overpredicts the modulus of short-fiber/particulate composites. The inverse rule of mixtures model, also called the parallel model, typically underpredicts the modulus of short-fiber/particulate composites.

The Halpin–Tsai equations are often used to predict the modulus of short-fiber composites.[22–25] To estimate the longitudinal and transverse moduli of aligned unidirectional (oriented) short-fiber composites, the following equations are used. Equation (3a) will be referred to in this study as the Halpin–Tsai oriented-fiber model.

$$\frac{E_L}{E_m} = \frac{1 + 2(l/d)\eta_L V_f}{1 - \eta_L V_f} \tag{3a}$$

$$\frac{E_T}{E_m} = \frac{1 + 2\eta_T V_f}{1 - \eta_T V_f} \tag{3b}$$

$$\eta_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(l/d)} \tag{3c}$$

$$\eta_T = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2} \tag{3d}$$

where E_L is the longitudinal composite tensile modulus, E_m is the matrix tensile modulus, E_f is the fiber (filler) tensile modulus, V_f is the fiber (filler) volume fraction of the filler, l is the filler length, and d is the filler diameter.

TABLE III
Values for A for Nielsen Model[26,27]

Filler type	Aspect ratio	A
Cubes	1	2
Spheres	1	1.5
Random fibers	2	1.58
Random fibers	4	2.08
Random fibers	6	2.80
Random fibers	10	4.93
Random fibers	15	8.38
Uniaxially oriented fibers	—	2 (L/D)

For a two-dimensional (2D) random orientation of fibers, the following relation, shown in eq. (4), is used.[22] For composites possessing a three-dimensional (3D) random orientation of fibers, eq. (5) is used to predict the composite tensile modulus.[23]

2D randomly oriented fiber

$$E_c = \frac{3}{8}E_L + \frac{5}{8}E_T \tag{4}$$

3D randomly oriented fiber

$$E_c = \frac{1}{5}E_L + \frac{4}{5}E_T \tag{5}$$

Nielsen's model is a macroscopic model that is the most versatile for conductive short-fiber/particulate composites. It accounts for constituent properties, concentrations of each constituent, as well as aspect ratio, orientation, and packing of the fillers. Nielsen's model, originally developed for a system containing one filler in one matrix material, constitutes the following series of equations.[26–29]

$$\frac{E_c}{E_m} = \frac{1 + ABV_f}{1 - B\Psi V_f} \tag{6a}$$

$$A = k_E - 1 \tag{6b}$$

$$B = \frac{(E_f/E_m) - 1}{(E_f/E_m) + A} \tag{6c}$$

$$\Psi \cong 1 + \frac{1 - \phi_m}{\phi_m^2}V_f \tag{6d}$$

where ϕ_m is the maximum packing fraction of the filler and k_E is the Einstein coefficient.

The constant A is related to the generalized Einstein coefficient and is a function of the aspect ratio and orientation (random versus unidirectional) of the filler. Table III shows the values for A for various types of fillers. Table IV shows the maximum packing frac-

TABLE IV
Values for Maximum Packing Fraction ϕ_m[26,27]

Filler shape	Type of packing	ϕ_m
Spheres	Hexagonal close	0.7405
Spheres	Face centered cubic	0.7405
Spheres	Body centered cubic	0.60
Spheres	Simple cubic	0.524
Spheres	Random loose	0.601
Spheres	Random close	0.637
Irregular particles	Random close	−0.637
Fibers	Three-dimensional random	0.52
Fibers	Uniaxial hexagonal close	0.907
Fibers	Uniaxial simple cubic	0.785
Fibers	Uniaxial random	0.82

tion ϕ_m of various types of filler shapes. The value of ϕ_m is based on particle shape (sphere, irregular particles, fibers) and packing order (random loose, random close, 3D random, etc.). When A approaches infinity and $\phi_m = 1$, then eq. (6a) becomes the rule of mixtures. This corresponds to the short-fiber/particulate conductive resin possessing its maximum possible modulus, that of a unidirectional continuous fiber composite. When A approaches zero and $\phi_m = 1$, Nielsen's model reduces to the inverse rule of mixtures. The factor B is used to take into account the relative modulus of the two components (one matrix and one filler). The factor Ψ is related to the maximum packing fraction of the filler. The quantity ΨV_f is similar to a reduced volume fraction, which approaches 1.0 when $V_f = \phi_m$.

McGee and McCullough proposed another equation, shown below, for Ψ.[28,30]

$$\Psi \cong 1 + \frac{V_m}{\phi_m}[\phi_m V_f + (1 - \phi_m)V_m] \tag{7}$$

Equation (7) was originally developed when studying the modulus of a natural silica in an epoxy resin and glass spheres in an epoxy resin. This equation will be referred to in this study as the modified Ψ term.

To take into account conductive resins with more than one filler, the following equations were used:

$$\frac{E_c}{E_1} = \frac{1 + \sum_{i=2}^{n} A_i B_i V_i}{1 - \sum_{i=2}^{n} B_i \Psi_i V_i} \tag{8a}$$

$$A_i = k_E - 1 \tag{8b}$$

$$B_i = \frac{(E_i/E_1) - 1}{(E_i/E_1) + A_i} \tag{8c}$$

$$\Psi_i \cong 1 + \frac{1 - \phi_{mi}}{\phi_{mi}^2} V_i \tag{8d}$$

$$\Psi_i \cong 1 + \frac{V_1}{\phi_{mi}}[\phi_{mi} V_i + (1 - \phi_{mi})V_1] \tag{8e}$$

where E_c is the composite tensile modulus, E_1 is the matrix tensile modulus, E_i is the tensile modulus of filler i (i = 2, 3, . . . , n), V_i is the volume fraction of filler i (i = 2, 3, . . . , n), V_1 is the volume fraction of matrix material, ϕ_{mi} is the maximum packing fraction of filler i (i = 2, 3, . . . , n), and k_E is the Einstein coefficient.

The subscript i represents the constituent where a subscript of 1 stands for the polymer matrix and greater subscripts (2, 3, ···) represent the different fillers. The shape factor A_i and maximum packing fraction ϕ_{mi} are both chosen for each filler used in a formulation. Thus for each filler used, there will be a separate term calculated for B and a separate term for Ψ.

RESULTS AND DISCUSSION

Filler length and aspect ratio results

Table V shows the mean length and aspect ratio (length/diameter) results of the synthetic graphite particles and carbon fibers for the factorial design formulations in both polymers after the fillers were

TABLE V
Mean Length and Aspect Ratio Results for Factorial Design Formulations

Formulation	Nylon 6,6		Polycarbonate	
	Length (μm)	Aspect ratio	Length (μm)	Aspect ratio
As-received carbon fibers (CF)	167.5	16.75	167.5	16.75
As-received Thermocarb™ (SG)	68.3	1.80	68.3	1.80
SG-only composites	70.6	1.68	46.9	1.67
SG-only replicate composites	68.5	1.70	47.7	1.67
CF-only composites	96.5	9.65	96.4	9.64
CF-only replicate composites	96.9	9.69	96.0	9.60
CF (SG + CF composites)	70.6	7.06	69.9	6.99
SG (SG + CF composites)	59.3	1.66	36.8	1.67
CF (SG + CF replicate composites)	70.1	7.01	70.1	7.01
SG (SG + CF replicate composites)	58.2	1.67	36.9	1.69

removed by solvent digestion. The values listed under the "as-received" formulation are the length and aspect ratio of the filler before extrusion and injection molding.

The results in Table V show there is significant degradation of the carbon fibers after the extrusion and injection-molding steps. The mean length and aspect ratio of the as-received carbon fibers was 167.5 and 16.75 μm, respectively. This compares well to the reported vendor literature value, which states a 200-μm mean carbon fiber length.[19] In the 20 wt % carbon fiber formulation in nylon 6,6, the fibers now have a mean length of 97 μm (aspect ratio = 9.7). In the nylon-based composites containing both carbon fibers and synthetic graphite, the mean length of the fibers was 70 μm (aspect ratio = 7.0). The fiber results for the polycarbonate-based composites were similar to those of the nylon composites, with the length decreasing to 96 μm (aspect ratio = 9.6) in the 20 wt % formulation, and then to a 70-μm length (aspect ratio = 7.0) in the composite containing fibers and synthetic graphite. Other researchers have reported similar carbon fiber lengths in nylon specimens that were also produced by extrusion and injection molding. These same researchers also noted that the carbon fiber length decreased as filler content increased.[31] This agrees with the results in this study that show that carbon fiber length decreased for the composites containing 20 wt % carbon fiber and 30 wt % synthetic graphite. Overall, processing reduced the carbon fiber length and aspect ratio to approximately half of its as-received values.

Table V also shows the lengths and aspect ratios of the synthetic graphite particles (Thermocarb TC-300 Specialty Graphite). Table V shows that the length and aspect ratio of the synthetic graphite particles in the composite specimens remains similar to that of the as-received material. This result is likely attributable to the relatively small length and aspect ratio of the as-received synthetic graphite. The as-received synthetic graphite has a mean length of 68 μm and a mean aspect ratio of 1.8. In the 30 wt % synthetic graphite formulation in nylon 6,6, the graphite particles now have a mean length of 70 μm (aspect ratio = 1.69). In the nylon-based composites containing both carbon fibers and synthetic graphite, the mean length of the synthetic graphite was 59 μm (aspect ratio = 1.67). The results for the polycarbonate-based composites were similar to those of the nylon composites, with the length decreasing to 47 μm (aspect ratio = 1.67) in the 30 wt % formulation, and to a 37-μm length (aspect ratio = 1.68) in the composite containing fibers and synthetic graphite.

Filler orientation results

As discussed previously, the filler orientation angle was measured by optical microscopy. The angle of interest in these measurements was the deviation of the filler away from the longitudinal tensile test direction, which is also the direction of polymer flow into the tensile test specimen mold. For these measurements, all of the angles will be between 0 and 90°. An angle of 0° signifies that the particles/fibers are aligned in the direction of flow into the mold, which is also the longitudinal tensile test direction. An angle of 90° means that a filler is oriented transverse to the direction of flow/tensile test.

Figure 3 shows the orientation results for the tensile samples containing 30 wt % Thermocarb TC-300 Specialty Graphite in nylon 6,6. The results in Figure 3 indicate that the fillers are primarily oriented in the longitudinal tensile test direction (more fillers found close to 0° orientation angle). For this formulation, the mean filler orientation angle was 28.4° with a standard deviation of 22.7° (769 particles measured). The results shown in Figure 3 were typical of all the formulations containing Thermocarb TC-300 Specialty Graphite.

For the tensile specimens containing 20 wt % carbon fiber in nylon, the mean filler orientation angle was 25.4° with a standard deviation of 23.8° (1433 fibers measured). Again, these results indicate that the fillers are primarily oriented in the longitudinal tensile test direction (more fillers found close to 0° orientation angle). The results were typical of all the formulations containing carbon fiber. Additionally, these results agree with those of other researchers who obtained similar distribution of orientation angles.[31–34]

Vibrated bulk density results

Table VI shows the mean VBD results for each single filler and each combination of fillers. For the combinations of fillers, the factorial design amounts were used.

Modeling results

Figures 4 and 5 show the mean tensile modulus (at least five specimens tested/formulation, standard deviation typically <5% of mean) of the composites containing varying amounts of a single carbon filler in nylon 6,6 and polycarbonate, respectively. The volume percentages shown in these figures correspond to the weight percentages given in Table II. Table VII lists the mean, standard deviation, and number of samples tested for the factorial design formulations. Because the factorial design formulations were produced twice, one column is labeled "original" and the other column is labeled "replicate."

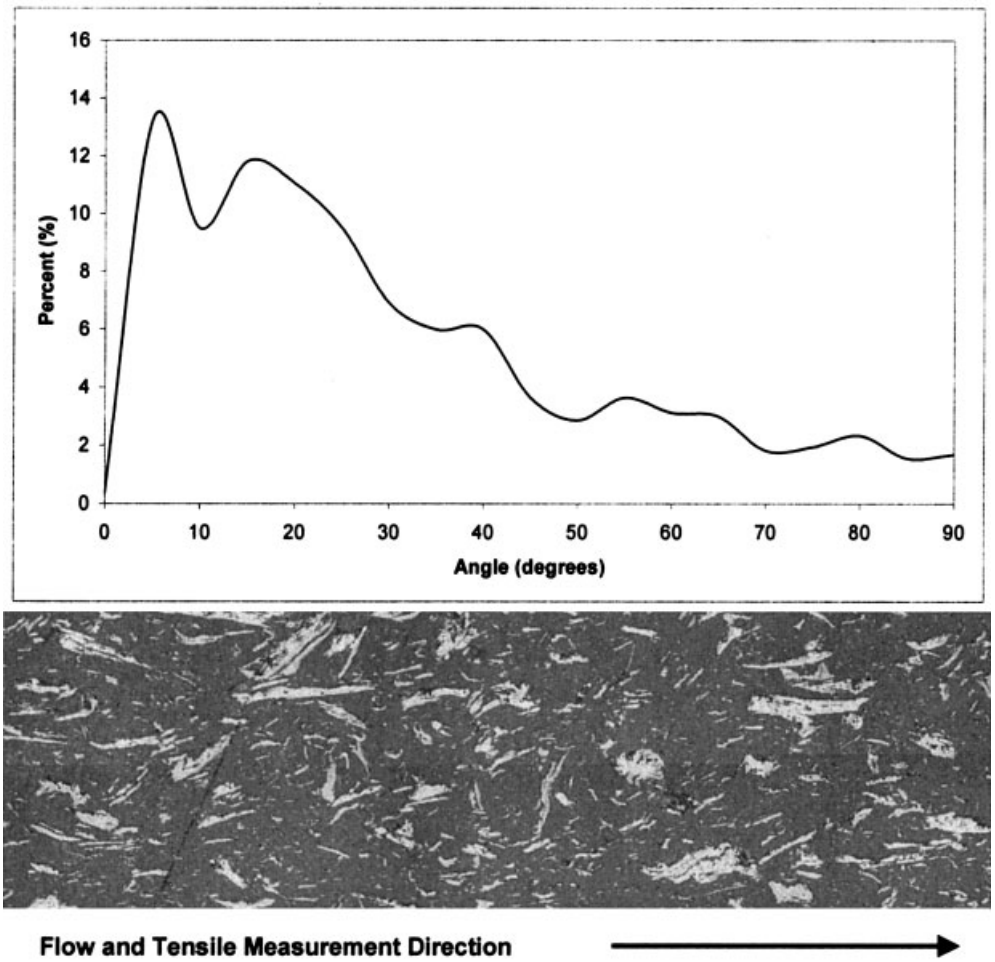

Figure 3 Orientation results for 30 wt % synthetic graphite in nylon 6,6 tensile specimen.

All the models discussed in this study require the tensile modulus of each constituent. According to the vendor literature, the tensile moduli of nylon 6,6 and polycarbonate were 3.100 and 2.356 GPa, respectively.[15,16] The tensile modulus of the Thermal-Graph DKD X carbon fiber was 827 GPa.[19] Because of the small size of the particles, tensile moduli were not available for synthetic graphite and carbon black. Because the carbon fiber and synthetic graphite (Thermocarb TC-300 Specialty Graphite) were both produced from petroleum pitch and were both graphitized, the tensile modulus of 827 GPa was also used for synthetic graphite. The structure of this electrically conductive carbon black consists of graphitic layers[35,36]; thus 827 GPa was used for the tensile modulus of Ketjenblack EC-600 JD.

TABLE VI
Filler-Vibrated Bulk Density

Filler	Vibrated bulk density (g/cm^3)
Carbon black	0.1082
Synthetic graphite	0.5330
Carbon fiber	0.2840
Carbon black + synthetic graphite	0.5101
Carbon black + carbon fiber	0.2575
Synthetic graphite + carbon fiber	0.4208
Carbon black + synthetic graphite + carbon fiber	0.3114

Basic and Halpin–Tsai tensile modulus models

Figure 6 shows the mean tensile modulus for the composites containing only carbon black in nylon along with the results predicted by using the inverse rule of mixtures and Halpin–Tsai models. The mean experimental values for the neat resin was 3.28 (original) and 3.30 (replicate) GPa compared to the vendor literature value of 3.10 GPa.[15] The models use the vendor literature results because these data are available to customers. Because carbon black is a sphere and not a fiber, 1.5 was used instead of $2(l/d)$ in the Halpin–Tsai equations.[26,27,35] Also, because of the spherical shape of the carbon black, all the Halpin–Tsai equations (oriented, 2D, and 3D) reduce to the same relation.

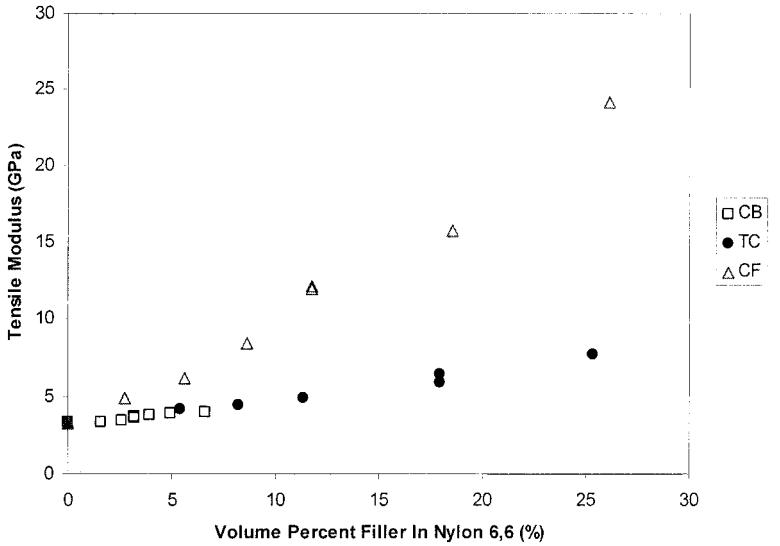

Figure 4 Tensile modulus of single-filler composites in nylon 6,6.

Figure 7 shows mean tensile modulus for the composites containing only synthetic graphite in nylon along with the results predicted by various models. For the Halpin–Tsai models, the aspect ratio (l/d) used for synthetic graphite was 1.68 (see Table V). Figure 8 shows the mean tensile modulus for the composites containing only carbon fiber in nylon along with the results predicted by the inverse rule of mixtures, Halpin–Tsai oriented model, Halpin–Tsai 2D randomly oriented model, and Halpin–Tsai 3D randomly oriented model. For the Halpin–Tsai models, the aspect ratio (l/d) used for carbon fiber was 9.6 (see Table V). From Figures 6, 7, and 8 several conclusions can be made. First, the rule of mixtures model typically predicts a tensile modulus 10 times that of the experimental value and thus the rule of mixtures model is not shown in these figures. Second, as expected, the inverse rule of mixtures model underestimated the experimental tensile modulus. Third, for the composites containing only synthetic graphite and the carbon fiber, the tensile modulus results predicted by the Halpin–Tsai oriented-fiber model were closest to the experimental data points for the three Halpin–Tsai models. This observation confirms the orientation results, which indicated that the fibers/particles were primarily oriented in the longitudinal tensile direction.

Nielsen's tensile modulus model

To use Nielsen's model, two parameters (A and ϕ_m) are chosen for each filler (see Tables III and IV). The parameters used are listed below. The aspect ratio (l/d) information from Table V was used for the composites containing synthetic graphite and carbon fiber.

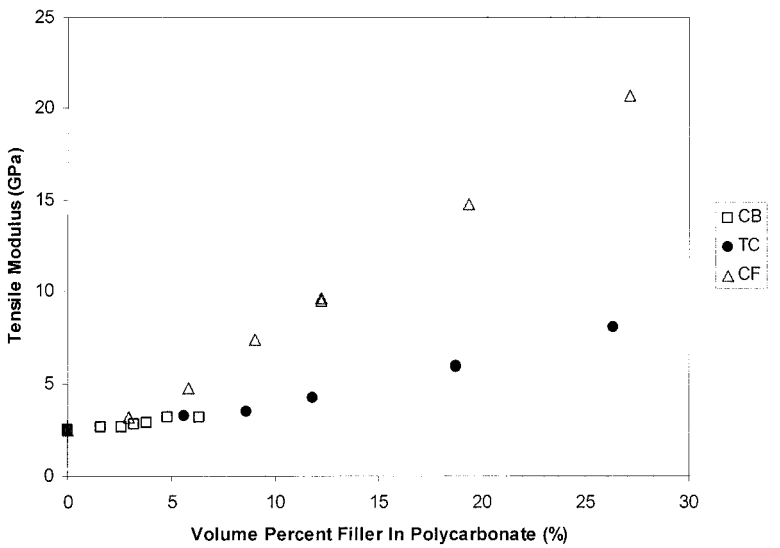

Figure 5 Tensile modulus of single-filler composites in polycarbonate.

TABLE VII
Tensile Modulus Results for Factorial Design Formulations in Nylon 6,6 and Polycarbonate

Formulation	Tensile modulus (GPa) Original[a]	Replicate[a]
Nylon 6,6		
No filler	3.28 ± 0.10 (5)	3.30 ± 0.15 (5)
CB	3.65 ± 0.09 (6)	3.71 ± 0.08 (5)
SG	5.91 ± 0.19 (6)	6.45 ± 0.04 (5)
CF	11.96 ± 0.79 (6)	12.14 ± 0.63 (5)
CB*SG	8.10 ± 0.70 (7)	8.16 ± 0.36 (6)
CB*CF	13.14 ± 0.81 (5)	12.03 ± 0.59 (7)
SG*CF	16.90 ± 1.17 (7)	16.82 ± 0.55 (5)
CB*SG*CF	25.23 ± 2.23 (7)	26.13 ± 2.34 (8)
Polycarbonate		
No filler	2.49 ± 0.05 (5)	2.46 ± 0.03 (6)
CB	2.81 ± 0.12 (5)	2.76 ± 0.12 (6)
SG	5.97 ± 0.15 (6)	5.87 ± 0.21 (8)
CF	9.62 ± 0.45 (5)	9.49 ± 0.52 (8)
CB*SG	7.40 ± 0.47 (8)	7.34 ± 0.30 (7)
CB*CF	10.22 ± 0.20 (5)	10.05 ± 0.37 (5)
SG*CF	17.66 ± 0.30 (5)	17.56 ± 0.28 (5)
CB*SG*CF	19.22 ± 0.24 (5)	19.35 ± 0.61 (5)

[a] n Values are in parentheses.

Carbon black

A = 1.5 (spherical filler)
ϕ_m = 0.637 (random close packing)

Synthetic graphite

$A = 2(l/d)$ (uniaxially oriented rods with aspect ratio = 1.68)
ϕ_m = 0.637 (random close irregular particles packing)

Carbon fiber

$A = 2(l/d)$ (uniaxially oriented fiber with aspect ratio = 9.6 for single-filler composites and 7.0 for multiple-filler composites)
ϕ_m = 0.82 (uniaxial random packing)

Figures 6, 7, and 8, discussed previously, also show the Nielsen model predictions. In every case, the Nielsen models provide the best estimate of composite tensile modulus. To determine the estimate for the Nielsen model with the original Ψ term, eqs. (6a)–(6d) were used. To determine the estimated value for the Nielsen model with the modified Ψ term, eqs. (6a), (6b), (6c), and (7) were used. The results for the composites containing only these single fillers in polycarbonate displayed the same trends as that presented in Figures 6, 7, and 8.

To quantitatively compare these models, two different goodness-of-fit parameters were calculated. The first term calculated was a standardized lack of fit term ϵ, which is shown below.

$$\varepsilon = \frac{\sum_i (y_i - y_{\mathrm{mod}_i})^2}{\sum_i y_i^2} \tag{9}$$

where y_i is the tensile modulus experimental result, y_{mod} is the tensile modulus result predicted by the model used, and i is the summation over all the different conductive resin formulations.

The second term was the sum of squares, which is the numerator shown in eq. (9). A value of zero for the sum of squares and ϵ would indicate a perfect fit of the

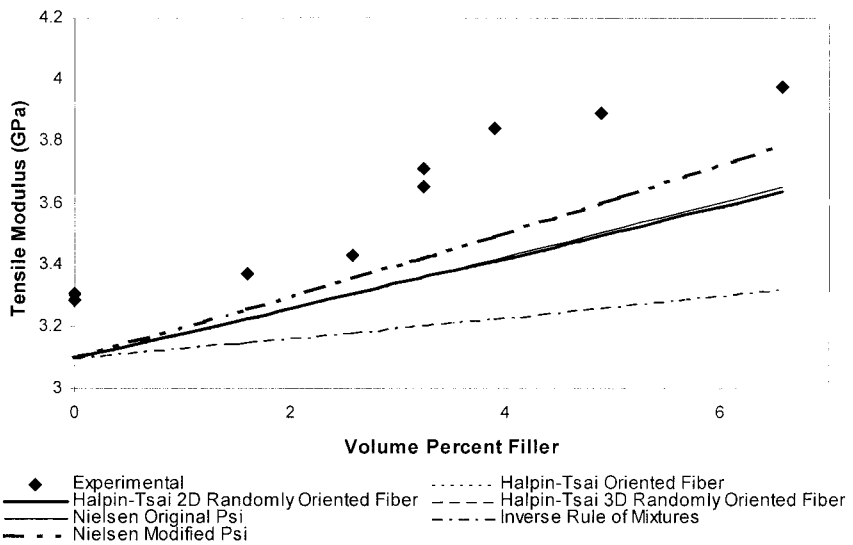

Figure 6 Inverse rule of mixtures, Halpin–Tsai, and Nielsen models and experimental results for composites containing only carbon black in nylon.

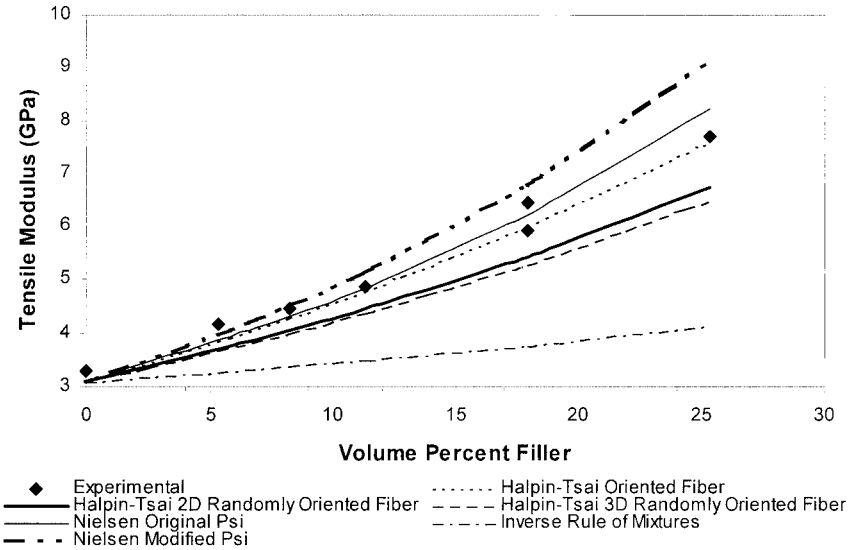

Figure 7 Inverse rule of mixtures, Halpin–Tsai, and Nielsen models and experimental results for composites containing only synthetic graphite in nylon.

experimental data with the model. Table VIII shows the comparison of the sum of squares and ϵ results for each model. This table illustrates that the Nielsen model with the modified Ψ term (given that this model has the lowest value for the sum of squares and ϵ) provides the best estimate of the experimental results.

Tensile modulus models for composites containing multiple fillers

Because the Nielsen model matched the experimental results the best, this model was used to predict the tensile modulus of the composites containing more than one type of filler. For the Nielsen model with the original Ψ term, eqs. (8a)–(8d) were used. For the Nielsen model with the modified Ψ term, eqs. (8a)–(8c), and (8e) were used. Table IX compares the results for the Nielsen models, the rule of mixtures, and inverse rule of mixtures models for these composites. This table shows that the standardized lack of fit term ϵ was 0.020 for the Nielsen model with the modified Ψ term. This was the lowest ϵ value for all the models discussed previously but was higher than that shown using the Nielsen model with the modified Ψ term for the composites containing only single fillers ($\epsilon = 0.005$ in Table VIII). Hence, a new model, based on the Nielsen model with the modified Ψ term, was proposed for composites containing more than one type

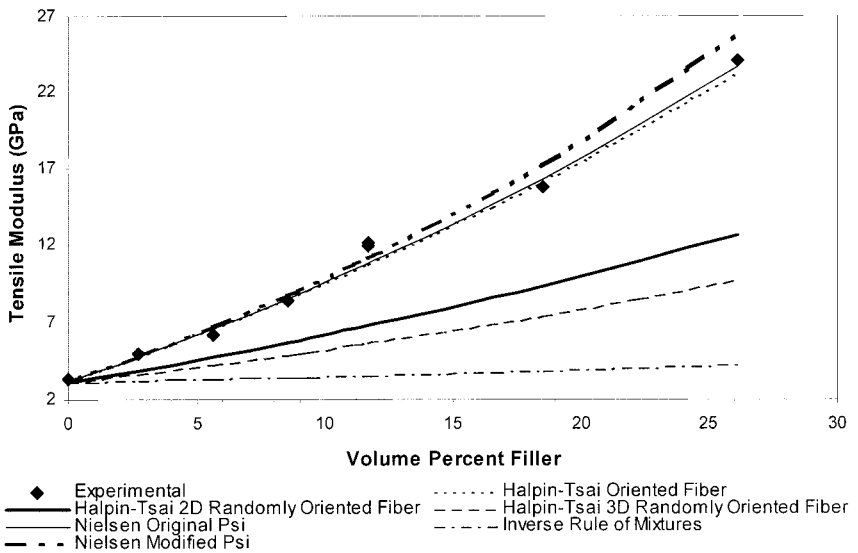

Figure 8 Inverse rule of mixtures, Halpin–Tsai, and Nielsen models and experimental results for composites containing only carbon fiber in nylon.

TABLE VIII
Comparison of Rule of Mixtures, Inverse Rule of Mixtures, Halpin–Tsai, and Nielsen Models for Single Fillers in Nylon and Polycarbonate

Model	Sum of squares $(GPa)^2$	ε
Rule of mixtures	387,251.12	138.594
Inverse rule of mixtures	1,366.12	0.489
Halpin–Tsai oriented fiber	24.06	0.009
Halpin–Tsai 2D	470.22	0.168
Halpin–Tsai 3D	716.89	0.257
Original Nielsen with original Ψ term	18.26	0.007
Nielsen model with modified Ψ term	14.99	0.005

of filler. Equations (10a) to (10e) below describe this model. Once again, the subscript i represents the constituent where a subscript of 1 stands for the polymer matrix and greater subscripts (2, 3, $\cdots$) represent the different fillers.

$$E_c = \sum_{i=2}^{n} E_1\left(\frac{1 + A_i B_i V_i}{1 - \Psi_i B_i V_i}\right) \tag{10a}$$

$$A_i = k_E - 1 \tag{10b}$$

$$B_i = \frac{(E_i/E_1) - 1}{(E_i/E_1) + A_i} \tag{10c}$$

$$\Psi_i \cong \mathrm{VBD}_C\left(1 + \frac{V_1}{\phi_{mi}}[\phi_{mi}V_i + (1 - \phi_{mi})V_1]\right) \tag{10d}$$

$$\mathrm{VBD}_C = \sum_{i=2}^{n}\left(\frac{V_i \mathrm{VBD}_i}{(1 - V_1)\mathrm{VBD}_{C\,\mathrm{measured}}}\right) \tag{10e}$$

where VBD_C is the vibrated bulk density correction term, VBD_i is the vibrated bulk density of component i, $\mathrm{VBD}_{C\,\mathrm{measured}}$ is the measured vibrated bulk density of composite (see Table VI: 0.5101 g/cm^3 for carbon black + synthetic graphite, 0.2575 g/cm^3 for carbon black + carbon fiber, 0.4208 g/cm^3 for synthetic graphite + carbon fiber, 0.3114 g/cm^3 for carbon black + synthetic graphite + carbon fiber), and V_i is the volume fraction of the filler component i.

This model incorporates the vibrated bulk density (VBD) measurements that are listed in Table VI. VBD is a measure of the filler packing. When combinations of different fillers are used, the VBD of the combination differs from that of the single filler. Because of the different filler shapes and sizes, smaller fillers can fall into the "gaps" between the larger fillers. Hence, the VBD_C term was developed to account for this difference. For a single-filler, eqs. (10a) to (10e) simplify to the Nielsen equation with the modified Ψ term [eqs. (6a)–(6c), and (7)]. Table IX shows that ϵ is reduced from 0.020 to 0.015 for all the composites containing multiple fillers when this VBD model with the modified Ψ term is used. Figure 9 displays this graphically for the composites containing multiple fillers in nylon. This figure shows that the predictions given by the VBD model more closely match the experimental results. The values at a total of 15.5 vol % filler contain carbon black and carbon fiber, the values at 22.1 vol % filler contain carbon black and synthetic graphite, the values at 34.1 vol % filler contain synthetic graphite and carbon fiber, and the values at 39.2 vol % filler contain carbon black, synthetic graphite, and carbon fiber. The results for the composites containing multiple fillers in polycarbonate displayed the same trends as that presented in Figure 9.

Table X compares the sum of squares and standardized lack-of-fit parameter ϵ for all the composites containing single and multiple fillers in nylon and polycarbonate. Table X indicates that the VBD model with modified Ψ term predicts the composite tensile modulus the best.

CONCLUSIONS

As a result of this study, the following conclusions can be made concerning the filler length, aspect ratio, and orientation. Extrusion and injection molding reduced the length and aspect ratio of the carbon fiber in the conductive composites to approximately half of its original length (168 μm) and aspect ratio (16.8). However, the length (typically 60 to 70 μm) and aspect ratio (typically 1.7 to 1.8) of the synthetic graphite particles in the composite specimens remain similar to those of the as-received material. This high-purity synthetic graphite likely maintained its size better compared to that of the carbon fiber because the as-received synthetic graphite particles have a smaller length and aspect ratio. Concerning orientation, because of the polymer flow into the mold during the injection-molding process, the synthetic graphite particles and carbon fibers are mainly oriented in the longitudinal tensile direction.

TABLE IX
Comparison of Rule of Mixtures, Inverse Rule of Mixtures, Nielsen, and VBD Models for Multiple Fillers in Nylon and Polycarbonate

Model	Sum of squares $(GPa)^2$	ε
Rule of mixtures	866,527.79	215.800
Inverse rule of mixtures	2,344.02	0.584
Original Nielsen with original Ψ term	164.13	0.041
Nielsen model with modified Ψ term	81.34	0.020
VBD with modified Ψ term	58.41	0.015

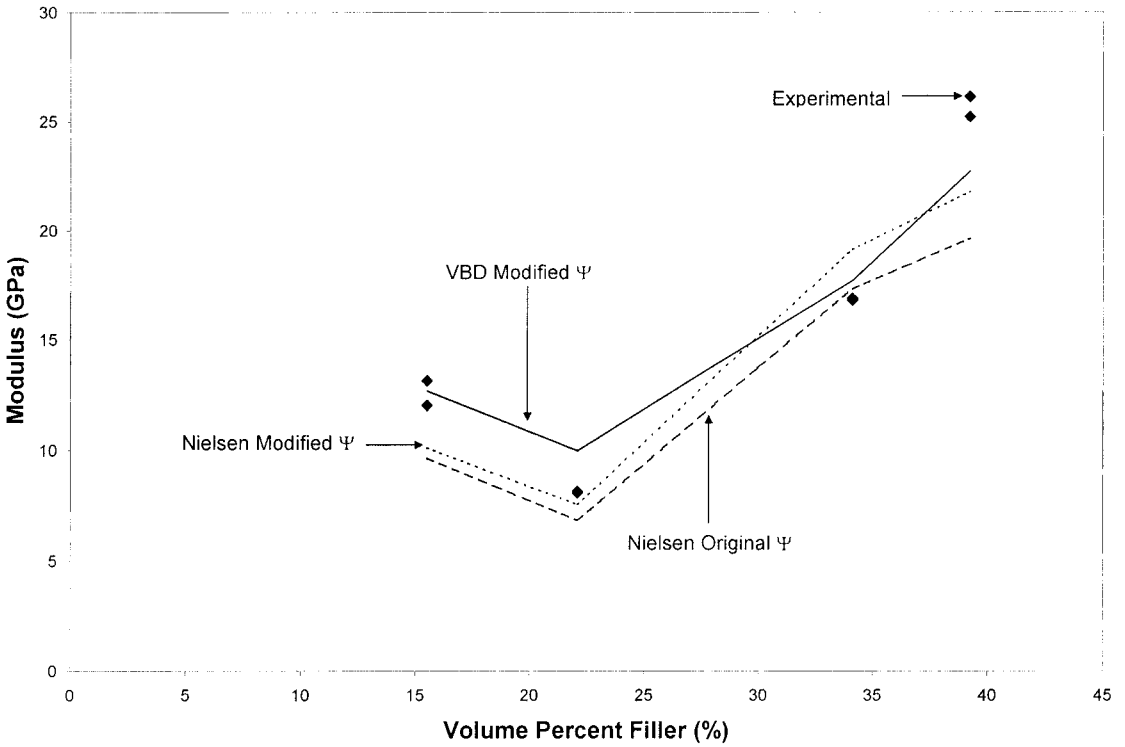

Figure 9 Nielsen and VBD models and experimental results for composites containing multiple fillers in nylon.

For the composites containing only one filler type, the Nielsen model with the modified Ψ term provided the best prediction of the actual experimental values. For the composites containing more than one filler type, a new parameter, which includes the vibrated bulk density (VBD) of the fillers, was incorporated into the Nielsen model with the modified Ψ term. This model provided the best estimate of the experimental tensile modulus. Thus, for composites containing multiple fillers the following model is proposed:

$$E_c = \sum_{i=2}^{n} E_1\left(\frac{1 + A_i B_i V_i}{1 - \Psi_i B_i V_i}\right) \tag{10a}$$

$$A_i = k_E - 1 \tag{10b}$$

TABLE X
Comparison of Rule of Mixtures, Inverse Rule of Mixtures, Nielsen, and VBD Models for All Formulations in Nylon and Polycarbonate

Model	Sum of squares $(GPa)^2$	ε
Rule of mixtures	1,253,778.91	115.823
Inverse rule of mixtures	3,710.14	0.343
Original Nielsen with original Ψ term	182.39	0.017
Nielsen model with modified Ψ term	96.34	0.009
VBD with modified Ψ term	73.40	0.007

$$B_i = \frac{(E_i/E_1) - 1}{(E_i/E_1) + A_i} \tag{10c}$$

$$\Psi_i \cong \mathrm{VBD}_C\left(1 + \frac{V_1}{\phi_{mi}}[\phi_{mi}V_i + (1 - \phi_{mi})V_1]\right) \tag{10d}$$

$$\mathrm{VBD}_C = \sum_{i=2}^{n}\left(\frac{V_i \mathrm{VBD}_i}{(1 - V_1)\mathrm{VBD}_{C\,\mathrm{measured}}}\right) \tag{10e}$$

Once again, the subscript i represents the constituent where a subscript of 1 stands for the polymer matrix and greater subscripts (2, 3, $\cdots$) represent the different fillers. Parameter B_i is calculated using eq. (10c). Parameter A_i is chosen for each filler using Table III. The maximum packing fraction ϕ_{mi} is chosen for each filler using Table IV.

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