

# Thermally Conductive Nylon 6,6 and Polycarbonate Based Resins. II. Modeling

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**ABSTRACT:** Increasing the thermal conductivity of typically insulating polymers opens new markets. A thermally conductive resin can be used for heat-sink applications. This research focused on extruding followed by injection molding and thermal conductivity 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, conductive 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 through-plane

thermal conductivity experimental results were then compared to results predicted by several different thermal conductivity models. An improved thermal conductivity model was developed that fit the experimental results well for resins that contained single fillers and combinations of different fillers. This improved model was based on the original Nielsen model. A single value for the shape parameter,  $A$  (which is needed in Nielsen's model), was used for all three different fillers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 123–130, 2003

**Key words:** composites; fillers; nylon; polycarbonates

## INTRODUCTION

Most polymer resins are thermally insulating. Increasing the thermal conductivity of these resins opens large, new markets. 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.

As stated in the companion article, there are many references in the literature concerning adding a conductive filler to a polymer matrix to produce a more conductive material.<sup>1</sup> There are also many thermal conductivity models discussed in the literature that predict the thermal conductivity of conductive resins.<sup>2,3</sup> These existing thermal conductivity models do not accurately predict the thermal conductivity of carbon-based short fiber/particulate composites, especially at high filler concentrations.

In this research, Michigan Technological University (MTU) performed compounding runs followed by injection molding and thermal conductivity testing of

carbon filled resins. Two different polymers were used: nylon 6,6 and polycarbonate. The three carbon fillers investigated included an electrically conductive carbon black, synthetic graphite particles, and a milled pitch based carbon fiber. For each polymer, 14 formulations were produced and tested that contained 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 article was to develop an improved thermal conductivity model for short fiber/particulate composites.

## MATERIALS AND EXPERIMENTAL METHODS

### Materials

Two matrix materials were utilized in this project. The first matrix used was DuPont Zytel 101 NC010, an unmodified semicrystalline nylon 6,6. The second matrix used was Lexan HF 1110-111N (clear in color), which is an amorphous engineering thermoplastic produced by GE Plastics. Three different carbon fillers were employed in this project. Akzo Nobel Ketjenblack EC-600 JD, an electrically conductive carbon black, was used. The second filler used was Thermo-carb™ TC-300 Specialty Graphite, a high-purity synthetic graphite that is available from Conoco Inc. The third filler used was BP/Amoco's pitch based milled (200 micron long) carbon fiber, ThermalGraph DKD X.

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The detailed vendor information on all the polymers and fillers used is described elsewhere.<sup>4</sup>

In this current study, a 2<sup>3</sup> factorial design (three factors or fillers in this case at two different loading levels) was conducted 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 zero 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. Composites containing varying amounts of a single filler were also produced. The following loading levels were used in both polymers.

Ketjenblack EC-600 JD: 2.5, 4.0, 5.0, 6.0, 7.5, and 10.0 wt %

Thermocarb TC-300 Specialty Graphite: 10.0, 15.0, 20.0, 30.0, and 40.0 wt %

ThermalGraph DKD X: 5.0, 10.0, 15.0, 20.0, 30.0, and 40.0 wt %

The companion article discusses these formulations in more detail, along with the fabrication and test methods used and all the through-plane thermal conductivity results.<sup>1</sup> This article focuses on using these through-plane thermal conductivity results to develop an improved thermal conductivity model for short fiber/particulate composites.

### THERMAL CONDUCTIVITY THEORY AND PREDICTIVE MODELS

For conductive resins, heat is transferred by two mechanisms, lattice vibrations (major contributor) and electron movement. Several key factors affect the thermal conductivity of a composite. These include the thermal conductivity of its constituents (filler and matrix) and the crystallinity of the polymer (increasing crystallinity improves polymer thermal conductivity). The filler size, shape, concentration, dispersion (degree of mixing), orientation, and bonding between the filler and the matrix also greatly affect thermal conductivity. Several researchers have shown that increasing the aspect ratio (length/diameter) of a carbon filler increases the conductivity of the conductive composite.<sup>5,6</sup> Due to packing phenomenon, it is possible to increase the maximum carbon concentration by mixing carbon fibers (high aspect ratio) and carbon particles (low aspect ratio). Obviously, increasing the conductive carbon filler content increases the conductivity of the resin.

Many thermal conductivity models are used to predict the thermal conductivity of a composite.<sup>2,7-9</sup> The three most basic models are shown below for a Three-component system (e.g., one matrix material and two different fillers).

$$K = \phi_1 k_1 + \phi_2 k_2 + \phi_3 k_3 \quad \text{Rule of Mixtures} \quad (1)$$

$$\frac{1}{K} = \frac{\phi_1}{k_1} + \frac{\phi_2}{k_2} + \frac{\phi_3}{k_3} \quad \text{Inverse Rule of Mixtures} \quad (2)$$

$$K = k_1^{\phi_1} k_2^{\phi_2} k_3^{\phi_3} \quad \text{Geometric Rule of Mixtures} \quad (3)$$

where  $K$  is the composite thermal conductivity;  $\phi_1$  is the volume fraction of component 1;  $\phi_2$  is the volume fraction of component 2;  $\phi_3$  is the volume fraction of component 3;  $k_1$  is the thermal conductivity of component 1;  $k_2$  is the thermal conductivity of component 2; and  $k_3$  is the thermal conductivity of component 3.

The rule of mixtures model [sometimes called the series model, eq. (1)] is the weighted average of matrix and fillers thermal conductivities. This model works well to predict the thermal conductivity of a unidirectional composite with continuous fibers but typically overpredicts the thermal conductivity of short fiber/particulate composites. The inverse rule of mixtures model (also called the parallel model) typically underpredicts the thermal conductivity of short fiber/particulate composites. The geometric rule of mixtures model (also called geometric mean model) typically fits the shape of the thermal conductivity data better than the first two models discussed.

Nielsen's model is a macroscopic model that is the most versatile for conductive short fiber/particulate composites.<sup>2,3,7,10</sup> It accounts for constituent thermal conductivities, concentrations of each constituent, as well as aspect ratio, orientation, and packing of the fillers. Nielsen's model was originally developed for a system containing one filler in one matrix material and is given below.<sup>3,7</sup>

$$\frac{K}{k_1} = \frac{1 + AB\phi_2}{1 - B\psi\phi_2} \quad (4a)$$

$$A = k_E - 1 \quad (4b)$$

$$B = \frac{k_2/k_1 - 1}{k_2/k_1 + A} \quad (4c)$$

$$\psi \cong 1 + \frac{1 - \phi_m}{\phi_m^2} \phi_2 \quad (4d)$$

where  $K$  is the composite thermal conductivity;  $k_1$  is the thermal conductivity of the matrix;  $k_2$  is the thermal conductivity of the filler;  $\phi_2$  is the volume fraction of the filler;  $\phi_m$  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 vs. unidirectional) of the filler. Table I, shows the values for  $A$  for various types of fillers. Table II shows the maximum packing fraction,  $\phi_m$ , of various types of filler shapes.  $\phi_m$  is based on

**TABLE I**  
Values for  $A$  for Nielsen Model<sup>3,7</sup>

| 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 | —            | $2L/D^a$ |
| Uniaxially oriented fibers | —            | $0.5^b$  |

<sup>a</sup> Heat flow in direction of fibers.

<sup>b</sup> Heat flow transverse to fiber direction.

particle shape (sphere, irregular particles, fibers) and packing order (random loose, random close, three dimensional random, etc.). When  $A$  approaches infinity and  $\phi_m = 1$ , then eq. (4a) becomes the rule of mixtures. This corresponds to the short fiber/particulate conductive resin possessing its maximum possible conductivity, 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 conductivity of the two components (one matrix and one filler). The factor  $\psi$  is related to the maximum packing fraction of the filler. The quantity  $\psi\phi_2$  is similar to a reduced volume fraction which approaches 1.0 when  $\phi_2 = \phi_m$ .

Nielsen's model has several limitations. For example, it typically underestimates the thermal conductivity at high filler concentrations. Agari et al. and King et al. have shown that at >25 vol % conductive filler, the actual thermal conductivity is a factor of two to three times higher than the value predicted by Nielsen's model.<sup>6,11</sup>

McGee and McCullough proposed another equation, shown below, for  $\psi$ .<sup>12,13</sup>

$$\psi \cong 1 + \frac{\phi_1}{\phi_m} [\phi_m \phi_2 + (1 - \phi_m) \phi_1] \quad (5)$$

Equation (5) 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 article as the modified  $\psi$  term.

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

$$\frac{K}{k_1} = \frac{1 + \sum_{i=2}^n A_i B_i \phi_i}{1 - \sum_{i=2}^n B_i \psi_i \phi_i} \quad (6a)$$

$$A_i = k_E - 1 \quad (6b)$$

$$B_i = \frac{k_i/k_1 - 1}{k_i/k_1 + A_i} \quad (6c)$$

$$\psi_i \cong 1 + \frac{1 - \phi_{mi}}{\phi_{mi}^2} \phi_i \quad (6d)$$

$$\psi_i \cong 1 + \frac{\phi_1}{\phi_{mi}} [\phi_{mi} \phi_i + (1 - \phi_{mi}) \phi_1] \quad (6e)$$

where  $K$  is the composite thermal conductivity;  $k_1$  is the thermal conductivity of the matrix;  $k_i$  is the thermal conductivity of filler  $i$  ( $i = 2, 3 \dots n$ );  $\phi_i$  is the volume fraction of filler  $i$  ( $i = 2, 3, \dots n$ );  $\phi_1$  is the volume fraction of matrix material;  $\phi_{mi}$  is the maximum packing fraction of filler  $i$ ; 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,  $\phi_{mi}$ , 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  $\psi$ .

## MODELING RESULTS

All the models discussed in this article require the thermal conductivity of each constituent. For this article, the following thermal conductivity values were used.<sup>4</sup> Nylon 6,6: 0.25 W/mK

Polycarbonate: 0.19 W/mK

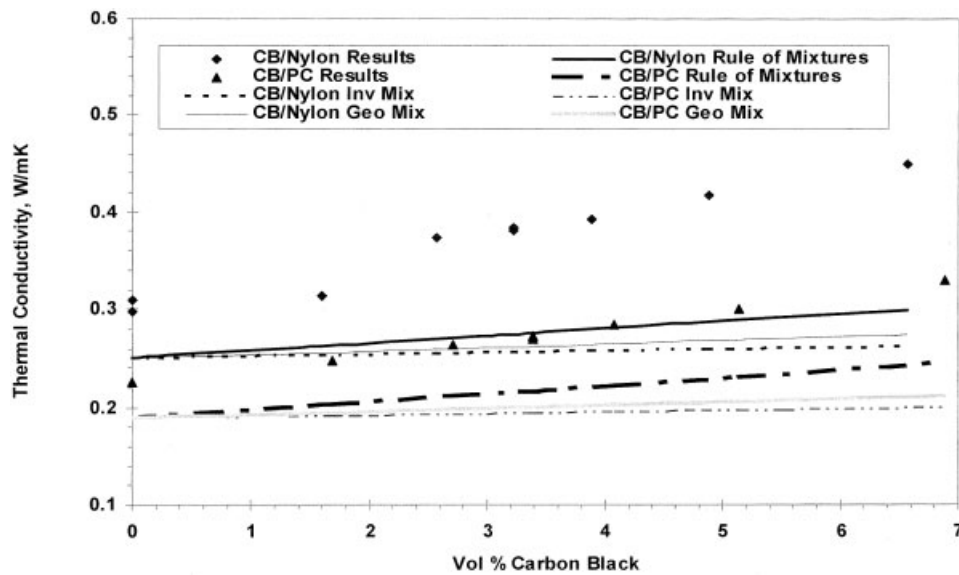
Ketjenblack EC-600 JD: 1. W/mK

Thermocarb TC-300 Specialty Graphite: 600. W/mK

ThermalGraph DKD X: 400. W/mK

**TABLE II**  
Values for Maximum Packing Fraction<sup>3,7</sup>

| Filler shape        | Type of packing          | $\phi_m$ |
|---------------------|--------------------------|----------|
| 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     |



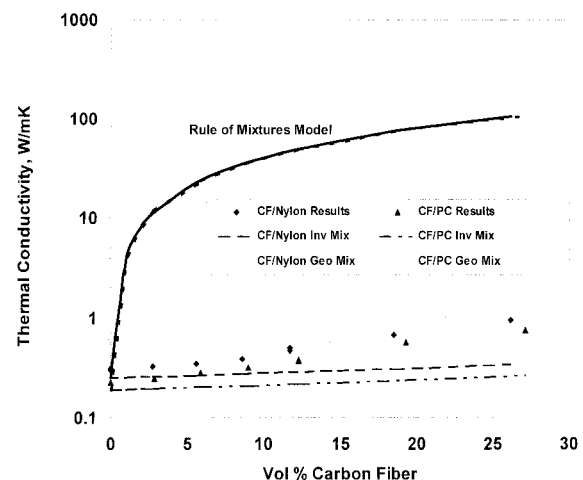
**Figure 1** Rule of mixtures, inverse rule of mixtures, and geometric rule of mixtures models and experimental results for composites containing only carbon black.

### Basic thermal conductivity models

Figure 1 shows the actual through-plane thermal conductivity data for the composites containing only carbon black (also abbreviated as CB in this article) along with the results predicted by using the rule of mixtures, the inverse rule of mixtures, and the geometric rule of mixtures models. In both polymers, the experimental results are higher than that predicted by the models. At the highest carbon black loading, the actual data is approximately 40% higher than that predicted by the rule of mixtures model. The inverse rule of mixtures model predicts lower values than the rule of mixtures model. In each polymer, the geometric rule of mixtures model predicts similar values to the inverse rule of mixtures model.

Figure 2 shows the actual through-plane thermal conductivity data for the composites containing only carbon fiber (also abbreviated as CF in this article) along with the results predicted by using the rule of mixtures, inverse rule of mixtures, and geometric rule of mixtures models. The rule of mixtures models in both polymers lie on top of each other in this figure. As expected, the model predicts a much higher value than obtained experimentally. Typically, the rule of mixtures model predicts thermal conductivity two orders of magnitude higher than the experimental results. The inverse rule of mixtures models predict values lower than the experimental data. Typically, the actual data is approximately three times higher than that predicted by the inverse rule of mixtures models. The geometric rule of mixtures model performs the best of these three basic models for the composites containing only carbon fiber. The geometric rule of mixtures model predicts values approximately twice that of the actual data.

When comparing the composites containing only synthetic graphite (also shown as SG in this article) and the composites containing more than one type of filler along with the results predicted by the rule of mixtures, inverse rule of mixtures, and geometric rule of mixtures models, results similar to that noted in Figure 2 are evident. In these cases, the rule of mixtures model predicts thermal conductivity two orders of magnitude higher than the experimental results and the inverse rule of mixtures predicts values much lower than the experimental results. The geometric rule of mixtures model performs the best of these three basic models. It overpredicts the actual data by approximately 60% for the composites containing high levels of only synthetic graphite. For the composites



**Figure 2** Rule of mixtures, inverse rule of mixtures, and geometric rule of mixtures models and experimental results for composites containing only carbon fiber.

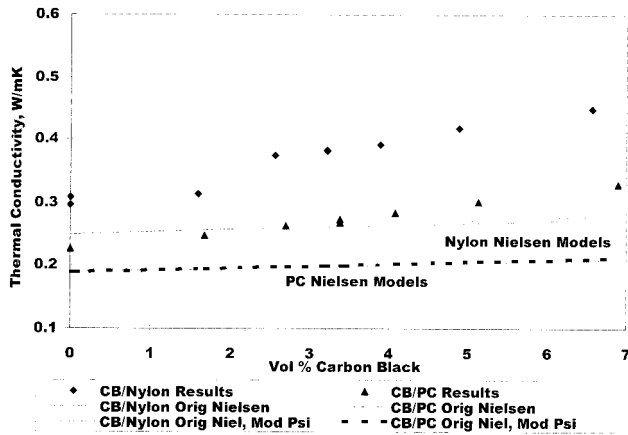


Figure 3 Original Nielsen model, original Nielsen model with modified  $\psi$ , and experimental data for composites containing only carbon black.

containing high levels of multiple fillers, the geometric rule of mixtures model predicts values approximately twice that of the actual data.

**Nielsen’s thermal conductivity model**

To use Nielsen’s model, two parameters ( $A$  and  $\phi_m$ ) are chosen for each filler (see Tables I and II). The parameters used are listed below. For the composites containing carbon fibers, the aspect ratio (length/diameter) of the fibers in the composite was 8 so  $A$  was chosen to match this aspect ratio:<sup>1</sup> Carbon Black:  $A = 1.5$  (spherical filler),  $\phi_m = 0.637$  (random close packing); Thermocarb Specialty Graphite:  $A = 1.58$  (rods with aspect ratio = 2),  $\phi_m = 0.637$  (random close irregular particles packing); Carbon Fiber:  $A = 3.74$  (fiber with aspect ratio = 8),  $\phi_m = 0.52$  (three dimensional random packing).

Figure 3 shows the actual through-plane thermal conductivity data for the composites containing only carbon black along with the results predicted by using Nielsen’s original model [eqs. (6a), (6c), and (6d)], and Nielsen’s model with the modified  $\psi$  term [eqs. (6a), (6c), and (6e)]. For each polymer, both of these models lie on top of each other. In fact, for both polymers, both Nielsen models and the geometric rule of mixtures model give essentially the same results. The actual data points are approximately 40% higher than that predicted by these models.

Figure 4 shows the actual through-plane thermal conductivity data for the composites containing only Thermocarb Specialty Graphite (a high-purity synthetic graphite) along with the results predicted by using Nielsen’s original model and Nielsen’s model with the modified  $\psi$  term. The two model lines nearer the top of the graph correspond to the predicted results for the nylon-based resins and the two model lines nearer the bottom of the graph correspond to the

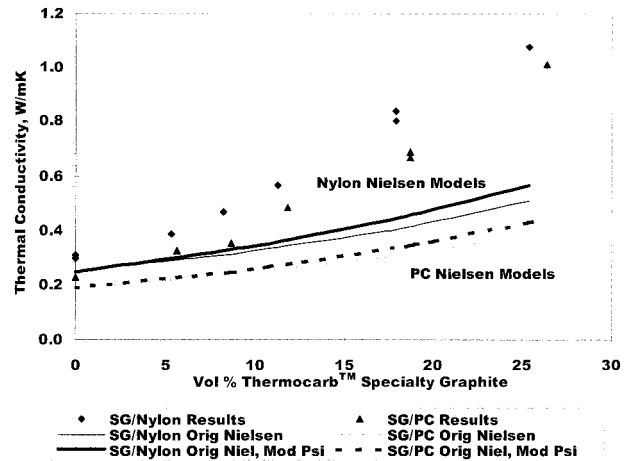


Figure 4 Original Nielsen model, original Nielsen model with modified  $\psi$ , and experimental data for composites containing only Thermocarb Specialty Graphite.

predicted results for the polycarbonate based resins. For each polymer, Nielsen’s model with the modified  $\psi$  term predicts the actual experimental results better than Nielsen’s model using his original  $\psi$  term. The actual results for both polymers are about twice that predicted by Nielsen’s model with the modified  $\psi$  term.

Figure 5 displays the actual through-plane thermal conductivity data for the composites containing only carbon fiber along with the results predicted by using Nielsen’s original model and Nielsen’s model with the modified  $\psi$  term. Again, the two model lines nearer the top of the graph correspond to the predicted results for the nylon-based resins and the two model lines nearer the bottom of the graph correspond to the predicted results for the polycarbonate-based resins. Once again for each polymer,

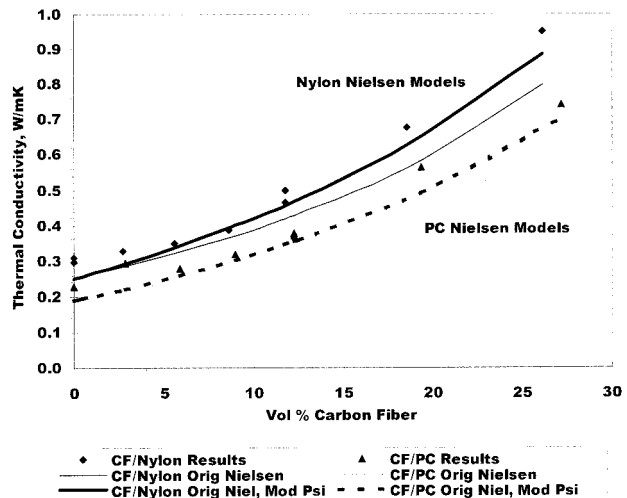
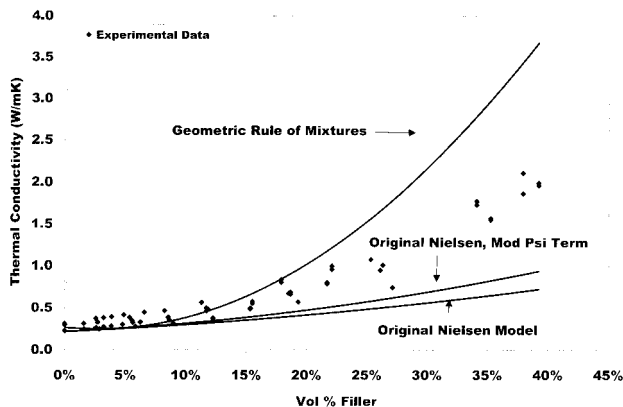


Figure 5 Original Nielsen model, original Nielsen model with modified  $\psi$ , and experimental data for composites containing only carbon fiber.



**Figure 6** Summary showing all experimental results in nylon and polycarbonate-based composites along with geometric rule of mixtures model, original Nielsen model, and original Nielsen model with modified  $\psi$  term.

Nielsen's model with the modified  $\psi$  term predicts the actual experimental results better than Nielsen's model using his original  $\psi$  term. At the highest filler level, the experimental results are roughly 10% higher than that predicted by Nielsen's model with the modified  $\psi$  term.

Figure 6 shows all the experimental results in nylon and polycarbonate-based composites along with the following models: geometric rule of mixtures, Nielsen's original model, and Nielsen's model with the modified  $\psi$  term. This graph shows that Nielsen's model with the modified  $\psi$  term appears to fit the experimental data the best. This model also has adjustable parameters ( $A$ ,  $\phi_m$ ) that could be used to optimize this model. The geometric rule of mixtures model does not have any adjustable parameters.

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

$$\epsilon = \frac{\sum_i (y_i - y_{\text{mod},i})^2}{\sum_i y_i^2} \quad (7)$$

where  $y_i$  is the through-plane thermal conductivity experimental result;  $y_{\text{mod}}$  is the through-plane thermal conductivity 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. (7). A value of zero for the sum of squares and  $\epsilon$  would indicate a perfect fit of the experimental data with the model. Table III shows the comparison of the sum of squares and  $\epsilon$  results for each model. This table illustrates that the Nielsen model with the modified  $\psi$  term (because this model

has the lowest value for the sum of squares and  $\epsilon$ ) provides the best fit with the experimental results.

### Optimization of Nielsen's thermal conductivity model

Nielsen's model has two parameters ( $A$ ,  $\phi_m$ ) that can be optimized for the particular filler used. The parameter  $A$  mainly depends on the filler shape and how the filler is oriented in the composite with respect to the direction of thermal conductivity measurement. The parameter  $\phi_m$  is the maximum filler packing fraction, which is defined as the true volume of the filler divided by the apparent volume occupied by the filler.<sup>3</sup> The first step taken in optimizing the Nielsen model was to determine which of these two parameters, or possibly both, to adjust to obtain a better fit of our experimental results. The entire through-plane thermal conductivity data set (60 formulations) was used.<sup>1</sup> Both Nielsen's original model with the original  $\psi$  term [eqs. (6a), (6c), and (6d)] and Nielsen's model with the modified  $\psi$  term [eqs. (6a), (6c), and (6e)] were studied. The software used for this analysis was Microsoft Excel's solver function. The factors  $A$  and  $\phi_m$  were optimized to minimize the values for the sum of squares and  $\epsilon$ . Both factors also were required to be a positive value ( $A$  is related to aspect ratio or filler shape, which must be a positive value and  $\phi_m$  is the filler maximum packing fraction that must be a positive value). In addition,  $\phi_m$  was required to be less than one because packing fractions greater than one are not physically possible.

An  $A$  factor was optimized for each filler and matrix combination, so that a different  $A$  factor was used for carbon fiber in nylon, and carbon fiber in polycarbonate, and so on. Both of these factors were optimized individually and in combination for the Nielsen model with the original  $\psi$  term and the Nielsen model with the modified  $\psi$  term. The results of these optimizations are listed in Table IV. This table contains the sum of squares (SS),  $\epsilon$ , and the optimized factors ( $A$  and  $\phi_m$ ). The  $A$  factor had the greatest effect on the model error, demonstrating that  $A$  has the greatest opportunity for model optimization. Optimizing the  $A$  factor for the Nielsen model with modified  $\psi$  term reduced the sum of squares from 10.27 to 0.59  $\text{W}^2/\text{m}^2\text{K}^2$  com-

**TABLE III**  
Comparison of Basic Models and Nielsen's Models

| Model                                      | Sum of squares<br>(W/mK) <sup>2</sup> | $\epsilon$ |
|--|---------------------------------------|------------|
| Rule of mixtures                           | 465,428.60                            | 11,039.78  |
| Inverse rule of mixtures                   | 22.93                                 | 0.54       |
| Geometric rule of mixtures                 | 20.76                                 | 0.49       |
| Original Nielsen with original $\psi$ term | 13.63                                 | 0.32       |
| Nielsen Model with Modified $\psi$ term    | 10.27                                 | 0.24       |

TABLE IV  
Optimization of Parameters A and  $\phi_m$

| Model                        | Optimized Parameter | SS (W/mK) <sup>1</sup> | $\epsilon$ | Term     | CB N  | SG N  | CF N | CB P | SG P  | CF P  |
|------------------------------|---------------------|------------------------|------------|----------|-------|-------|------|------|-------|-------|
| Nielsen with original $\psi$ | None                | 13.63                  | 0.323      | A        | 1.50  | 1.58  | 3.74 | 1.50 | 1.58  | 3.74  |
|                              |                     |                        |            | $\phi_m$ | 0.64  | 0.64  | 0.52 | 0.64 | 0.64  | 0.52  |
| Nielsen with original $\psi$ | A                   | 0.89                   | 0.021      | A        | 1528  | 10.56 | 8.24 | 0.00 | 13.26 | 10.06 |
|                              |                     |                        |            | $\phi_m$ | 0.64  | 0.64  | 0.52 | 0.64 | 0.64  | 0.52  |
| Nielsen with original $\psi$ | $\phi_m$            | 1.96                   | 0.046      | A        | 1.50  | 1.58  | 3.74 | 1.50 | 1.58  | 3.74  |
|                              |                     |                        |            | $\phi_m$ | 0.12  | 0.30  | 0.52 | 0.08 | 0.30  | 1.00  |
| Nielsen with original $\psi$ | A, $\phi_m$         | 0.25                   | 0.006      | A        | 18.47 | 7.81  | 8.01 | 5.93 | 7.52  | 8.64  |
|                              |                     |                        |            | $\phi_m$ | 1.00  | 0.45  | 0.54 | 0.09 | 0.40  | 0.65  |
| Nielsen with modified $\psi$ | None                | 10.27                  | 0.244      | A        | 1.50  | 1.58  | 3.74 | 1.50 | 1.58  | 3.74  |
|                              |                     |                        |            | $\phi_m$ | 0.64  | 0.64  | 0.52 | 0.64 | 0.64  | 0.52  |
| Nielsen with modified $\psi$ | A                   | 0.59                   | 0.014      | A        | 2558  | 9.59  | 4.13 | 0.00 | 12.25 | 5.02  |
|                              |                     |                        |            | $\phi_m$ | 0.64  | 0.64  | 0.52 | 0.64 | 0.64  | 0.52  |
| Nielsen with modified $\psi$ | $\phi_m$            | 1.19                   | 0.028      | A        | 1.50  | 1.58  | 3.74 | 1.50 | 1.58  | 3.74  |
|                              |                     |                        |            | $\phi_m$ | 1.00  | 0.31  | 0.58 | 0.11 | 0.31  | 0.94  |
| Nielsen with modified $\psi$ | A, $\phi_m$         | 0.17                   | 0.004      | A        | 3245  | 9.89  | 3.98 | 2699 | 8.89  | 4.00  |
|                              |                     |                        |            | $\phi_m$ | 0.01  | 0.96  | 0.52 | 0.00 | 0.49  | 0.00  |

In this table, nylon-based composites are represented by “N” and polycarbonate-based composites are represented by “P.” For example, “CB N” stands for carbon black in nylon and “CB P” stands for carbon black in polycarbonate.

pared to 1.19 for optimizing  $\phi_m$ . Optimizing both A and  $\phi_m$  for the Nielsen model with the modified  $\psi$  term did reduce the sum of squares further to 0.17 W<sup>2</sup>/m<sup>2</sup>K<sup>2</sup>. Because  $\phi_m$  represents the maximum filler packing fraction, which has physical significance for each filler, the authors decided to use  $\phi_m$  as defined by the original Nielsen model (Table II) and focus on optimizing only the A parameter.

The first option that was studied was using a global (or single) A term for the three carbon-based fillers used in this study. A global A term might improve the model, allowing a first prediction of the filler loading to get a desired thermal conductivity, which could require fewer composite formulations to be fabricated. This option was investigated for the following cases using only the Nielsen model with the modified  $\psi$  term. (a) The entire data set: 60 composite formulations used for the model; (b) carbon black formulations removed: 34 composite formulations included for the model; (c) filler mixtures (more than one type of filler used) formulations removed: 44 composite formulations used for the model; (d) filler mixtures and carbon black formulations removed: 30 composite formulations used for the model.

The case with the carbon black formulations removed was considered because the fitted A terms for the carbon black from the previous analysis had significantly different values (range is 1.5 to 3245 in Table IV) compared to the other two fillers (range is 1.58 to 13.26 in Table IV). This was likely due to the fact that carbon black is substantially different from the other two fillers. Carbon black is extremely small (aggregates are 30–100 nm in size) compared to carbon fiber and Thermocarb Specialty Graphite, which are typically 50–100 microns in length. Carbon black structure

is also highly branched and has a much larger surface area as compared to the other fillers.<sup>1</sup> The possibility of removing the formulations that contained more than one type of filler (or filler mixtures) was also considered because the mixture formulations contributed to a substantial portion of the model’s error in predicting thermal conductivity.

The results of this study are shown in Table V. This table presents the  $\epsilon$  value for each case and the resulting global A term. The sum of squares is not included in this table because it is dependent on the number of formulations considered in each case, whereas the  $\epsilon$  value is not. Hence, the  $\epsilon$  value was the only parameter used to judge goodness of fit. In Table V, case 1 shows the results when using the Nielsen model with the modified  $\psi$  term and the original values for A and  $\phi_m$  (see Tables I and II). Case 1 has the largest  $\epsilon$  value (0.244) in this table. As a comparison to the global A cases, case 2 shows the lowest  $\epsilon$  value (0.014) when the Nielsen model with the modified  $\psi$  term, the original  $\phi_m$  value (see Table II), and different values for A are used for each filler/polymer combination (Table IV). Case 3 gives an  $\epsilon$  value of 0.040 (only case 2 has a lower  $\epsilon$  value). For case 3, the entire data set was used with all 60 formulations studied. Because cases 4–8 resulted in a higher  $\epsilon$  value, the authors decided to use all 60 formulations with the single (global) A value (case 3). Figure 7 shows the through-plane thermal conductivity results for all 60 formulations along with the model predictions using (a) the Nielsen model with the modified  $\psi$  term and original values of A and  $\phi_m$  from Tables I and II; and (b) the Nielsen model with the modified  $\psi$  term and original value of  $\phi_m$  from Table II and a single value for A of 7.8. This

TABLE V  
Global A Modification to the Nielsen Model with the Modified  $\psi$  Term and Using Original Values for  $\phi_m$

| Case no. | Formulations studied   | $\varepsilon$ | Global A |
|----------|--|---------------|----------|
| 1        | Original Nielsen, modified $\psi$ , original A and $\phi_m$ , all 60 formulations considered<br>Orig Nielsen, mod $\psi$ , orig $\phi_m$ , different "A" for each combination: all 60 formulations used  | 0.244         | —        |
| 2        | Orig Nielsen, mod $\psi$ , orig $\phi_m$ , same A used for all fillers: all 60 formulations used   | 0.014         | —        |
| 3        | Orig Nielsen, mod $\psi$ , orig $\phi_m$ , same A used for all fillers: Only 34 formulations studied (removed any formulation containing carbon black) in both polymers  | 0.040         | 7.80     |
| 4        | Orig Nielsen, mod $\psi$ , orig $\phi_m$ , same A used for all fillers: formulations considered that contained only synthetic graphite as a single filler and only carbon fiber as a single filler   | 0.049         | 7.25     |
| 5        | Orig Nielsen, mod $\psi$ , orig $\phi_m$ , same A used from case 5: only 34 formulations studied (removed any formulation containing carbon black)   | 0.050         | 5.37     |
| 6        | Orig Nielsen, mod $\psi$ , orig $\phi_m$ , same A used for all fillers: formulations used that contained only carbon black as a single filler, only synthetic graphite as a single filler, and only carbon fiber as a single filler in both polymers | 0.075         | 5.37     |
| 7        | Orig Nielsen, mod $\psi$ , orig $\phi_m$ , same A used from case 7: all 60 formulations studied  | 0.055         | 5.43     |
| 8        |  | 0.078         | 5.43     |

figures shows that that this updated Nielsen model matches the experimental data well.

### CONCLUSIONS

As a result of this study, the following model is proposed for composites containing carbon fillers, especially carbon black, synthetic graphite particles, and carbon fiber.

$$\frac{K}{k_1} = \frac{1 + A \sum_{i=2}^n B_i \phi_i}{1 - \sum_{i=2}^n B_i \psi_i \phi_i} \quad (8)$$

Once again, the subscript  $i$  represents the constituent where a subscript of 1 stands for the polymer

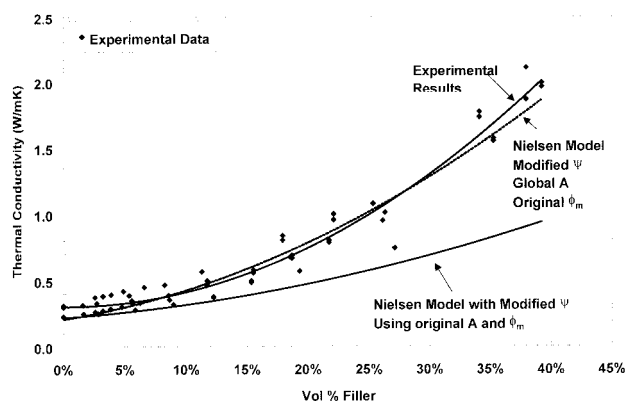


Figure 7 Comparison of the Nielsen model with the modified  $\psi$  term and original values of A and  $\phi_{mi}$ , Nielsen model with modified  $\psi$ , and global A and original value of  $\phi_{mi}$ , and experimental through-plane thermal conductivity results for all nylon and polycarbonate-based resins.

matrix and greater subscripts (2, 3, ...) represent the different fillers. Parameter  $B_i$  is calculated using eq. (6c). Parameter  $\psi_i$  is calculated using eq. (6e) (modified  $\psi$  equation). The maximum packing fraction,  $\phi_{mi}$ , is chosen for each filler using Table II. One value for A (7.8) is used for all the fillers and filler combinations.

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