Thermally Conductive Nylon 6,6 and Polycarbonate Based Resins. I. Synergistic Effects of Carbon Fillers

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ABSTRACT: Increasing the thermal conductivity of typically insulating polymers, such as nylon 6,6, opens new markets. A thermally conductive resin can be used for heat-sink applications. This research focused on performing compounding runs 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. The objective of this article was to determine the effects and interactions of each filler on the thermal conductivity properties of the conductive resins. From the through-plane thermal conductivity results, it was determined that for both nylon 6,6 and polycarbonate based resins, synthetic graphite particles caused the largest increase in composite thermal conductivity, followed by carbon fibers. The combination of synthetic graphite particles and carbon fiber had the third most important effect on composite thermal conductivity. J Appl Polym Sci 88: 112–122, 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 as 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.

Typical thermal conductivity values for some common materials are 0.2 to 0.3 for polymers, 234 for aluminum, 400 for copper, and 600 for graphite (all values in W/mK). One approach to improving the thermal conductivity of a polymer is through the addition of a conductive filler material, such as carbon and metal. Conductive resins with a thermal conductivity from approximately 1 to 30 W/mK can be used in heat-sink applications.[1]

There are many references in the literature concerning adding a conductive filler to a polymer matrix to produce a more thermally and electrically conductive material. For example, ceramic fibers/particles (boron nitride, aluminum nitride, aluminum oxide), metal fibers/particles (aluminum, steel, iron, copper, silver) and Ni-coated glass fibers have been used.[1–6] Metallic fillers have several disadvantages, relative to carbon, which include higher density and greater susceptibility to oxidation. Various types of carbons have been effective conductive fillers. For example, adding synthetic graphite to nylon 6,6 increases the thermal conductivity from approximately 0.3 to 1 W/mK.[7] Carbon black and carbon fiber have also been used.[1,8–16] Carbon black fillers have been successfully used to improve electrical conductivity, but these materials often have relatively low thermal conductivity. Carbon fibers, on the other hand, do improve both the thermal and electrical conductivities.

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. This project had two goals. The first goal, which is the focus of this article, was to determine the effects and interactions of each filler on the

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

Formulations	Ketjenblack EC-600 JD, wt %	Thermocarb™ speciality 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

thermal conductivity properties of the conductive resins. The second goal, which is discussed in the companion article, was to develop an improved thermal conductivity model for conductive composites containing short fibers/particles.[17]

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 polymer of medium viscosity. The second matrix used was Lexan HF 1110-111N (clear in color), which is an amorphous engineering thermoplastic produced by GE Plastics. The properties of these polymers are discussed elsewhere.[18–20]

Three different carbon fillers were employed in this project. Akzo 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 and slightly improved thermal conductivity in a composite. Also, carbon black has a large surface area, and hence, can contact a large amount of polymer.[21] Carbon black was selected as a filler because electrical conductivity was needed for another portion of this project that investigated electrically conductive composites. This current article focuses on thermal conductivity. Thermocarb™ TC-300 Specialty Graphite, a high-quality synthetic graphite, which is available from Conoco Inc., was used due to its high thermal conductivity and moderately high electrical conductivity.[22] BP/Amoco's pitch based milled (200 micron long) carbon fiber, ThermalGraph DKD X, was used to improve the electrical and thermal conductivity and the tensile strength of the resin.[23] The properties of these fillers are described elsewhere.[20–23]

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 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. Table I shows the factorial design formulations. In Table I, "CB" signifies carbon black, "SG" signifies synthetic graphite (Thermocarb), and "CF" signifies carbon fiber. Because this project focuses 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.

Thermal conductivity was 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 indirect heated dehumidifying drying oven and then stored in moisture barrier bags.

The extruder used was an American Leistritz Extruder Corporation Model ZSE 27. This extruder has a 27mm corotating intermeshing twin screw with 10 zones and a length/diameter ratio of 40. The screw design was chosen to obtain the maximum possible conductivity. Hence, a minimum amount of filler degradation was desired, while still dispersing the fillers well in the polymers. The polymer pellets (Zytel or Lexan) were introduced in Zone 1. The first side stuffer, utilized 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™ 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

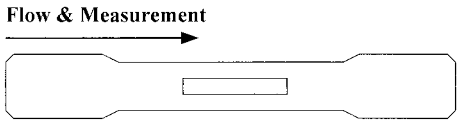

Figure 1 Portion of the tensile bar from which in-plane thermal conductivity specimen is cut.

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 prior to 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) and 6.4-cm diameter disks. The thermal conductivity of all molded formulations were determined.

Through-plane thermal conductivity test method

The through-plane thermal conductivity of a 3.2 mm thick, 5-cm diameter disc-shaped test specimen was measured at 55°C using a Holometrix Model TCA-300 Thermal Conductivity Analyzer, which uses ASTM F433 guarded heat flow meter method.[24] The nylon 6,6-based samples were all tested dry as molded (DAM). The polycarbonate based samples were conditioned at 50% RH for 24 hs at 23°C prior to testing. For each formulation, at least four samples were tested.

In-plane thermal conductivity test method

Typically one in-plane thermal conductivity specimen (4.8 mm wide × 3.2 mm high × 30.5mm long, rectangular shaped) was cut (along the length of the tensile bar) from the center necked portion of a tensile bar, as shown in Figure 1. Figure 2 illustrates the prepared

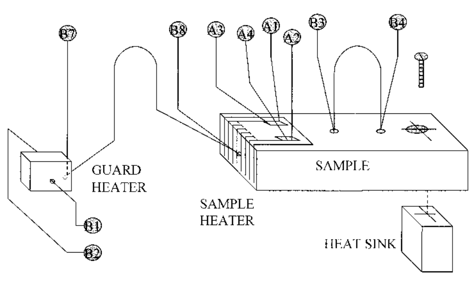

Figure 2 In-plane thermal conductivity wiring diagram.

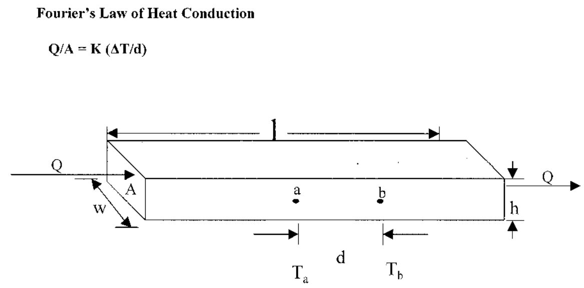

Figure 3 In-plane thermal conductivity theory.

in-plane thermal conductivity test specimen. The "A" and "B" markings on Figure 2 indicate wiring information. To prepare the in-plane thermal conductivity sample, several steps are needed. First, a sample heater (350 ohm strain gauge, type CEA-06-125UW-350 from Micro Measurements) is glued on one end of the specimen. This heater maintains the temperature at 45°C on this end of the specimen. On the other end of the in-plane thermal conductivity specimen, a hole is drilled, which will allow a screw to attach the "cold" end of the specimen to the cold sink, which is a copper block. In the center of the specimen, two thermocouples (type K) are placed that are 7.9 mm apart (B3-B4 connection in Fig. 2). These thermocouples are used to measure the specimen temperature difference.

The in-plane thermal conductivity test method is based on the four-probe method.[11] Axel Demain built this apparatus.[11] The goal is to conduct heat only by conduction through the solid sample. To minimize gaseous conduction, the entire system is evacuated to approximately 5×10^{-4} Torr. To minimize radiation heat losses, a heated guard surrounds the sample. The apparatus is operated such that there is no temperature difference between the sample heater and the guard heater. When the sample is energized, the generated heat flows through the sample from the sample heater to the cold sink. Heat is generated in the sample from electrical resistance heating of the sample heater. Thus, heat (Q) is equal to the power dissipated by the resistor ($V \times I$). Figure 3 illustrates this test method. Using Fourier's law, the thermal conductivity of the specimen is determined by the following equation:[11]

$$K = \frac{(V)(I)}{\Delta T}\left(\frac{d}{A}\right)$$

where K is the thermal conductivity of the specimen being tested; V is the voltage drop across the sample heater resistor; I is the current through the sample heater resistor; ΔT is the temperature difference across the specimen being tested, $T_a - T_b$ in Figure 3; d is the distance between the two junctions of the thermocouples (typically 7.9 mm); and A is the cross-sectional

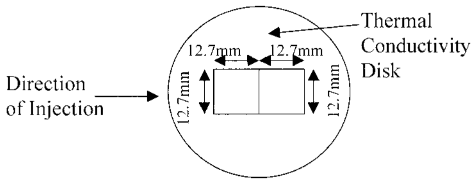

Figure 4 Diagram showing location of image analysis specimens.

area of the specimen (specimen width × specimen height).

Typically for each specimen, it takes 2 h to prepare a sample and 2 h to conduct the testing. Because this test is quite time consuming, in-plane thermal conductivity testing was only conducted on selected formulations. Again, the nylon 6,6-based samples were tested dry as molded (DAM). The polycarbonate based samples were conditioned at 50% RH for 24 h at 23°C prior to testing.

Filler length and aspect ratio test method

To determine the length of the carbon fiber and synthetic graphite in the thermal conductivity test specimens, solvent digestion was used. A 0.2-g sample cut from the center of a through-plane thermal conductivity test specimen was dissolved at 23°C using formic acid to remove the nylon 6,6 and methylene chloride to remove the polycarbonte. 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 1000 and 6000 particles/fibers were measured. Due to the extremely small size of the carbon black, the length and aspect ratio of the carbon black was not measured.

Filler orientation test method

To determine the orientation of the carbon fillers, a polished composite sample was viewed using an optical microscope. Again, due to the small size of the carbon black (aggregates 30 to 100 nm in size), the orientation of only the synthetic graphite particles and carbon fibers were determined. Two 13 × 13-mm squares were cut from the center of each through-plane thermal conductivity sample, as shown in Figure 4. These samples were cast in two part epoxy plugs such that two different images (one exposes the through the sample thickness 3.2-mm face) could be viewed, as shown in Figure 5. For the in-plane thermal conductivity samples, a similar method was used. The samples were then polished and viewed using an Olympus BX60 transmitted 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 using viewing typically 3,000 to 6,000 particles/fibers.

RESULTS

Filler-length and aspect ratio results

Table III 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 removed via solvent digestion. The values listed under the "as-received" formulation are the length and aspect ratio of the filler prior to extrusion and injection molding.

The results in Table III show there is significant degradation of the carbon fibers following the extrusion and injection molding steps. The mean length and aspect ratio of the as-received carbon fibers was 167.5 microns and 16.75, respectively. This compares well to the reported vendor literature value which states a 200 micron mean carbon fiber length.[23] In the 20 wt % carbon fiber formulation in nylon 6,6, the fibers now have a mean length of 95 microns (aspect ratio = 9.5). In the nylon-based composites containing both carbon fibers and synthetic graphite, the mean length of the fibers was 77 microns (aspect ratio = 7.7). The fiber results for the polycarbonate based composites were similar to those of the nylon composites, with the length decreasing to 82 microns (aspect ratio = 8.2) in the 20 wt % formulation, and then to a 71-micron length (aspect ratio = 7.1) in the composite containing fibers and synthetic graphite. Overall, processing reduced the carbon fiber length and aspect ratio to approximately half of its as received values.

Table III also shows the lengths and aspect ratios of the synthetic graphite particles (Thermocarb Specialty Graphite). Table III shows that the length and aspect ratio of the synthetic graphite particles in the composite specimens remain similar to that of the as received

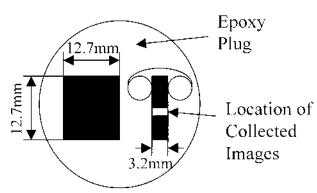

Figure 5 Diagram showing where images collected on through-plane thermal conductivity samples.

TABLE III
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 synthetic graphite (SG)	68.3	1.80	68.3	1.80
SG only composites	74.8	1.68	42.6	1.66
SG only replicate composites	56.0	1.61	49.7	1.70
CF only composites	95.7	9.57	85.7	8.57
CF only replicate composites	94.1	9.41	78.3	7.83
CF (SG*CF composites)	71.7	7.17	71.4	7.14
SG (SG*CF composites)	59.7	1.84	33.6	1.67
CF (SG*CF replicate composites)	82.3	8.23	70.8	7.08
SG (SG*CF replicate composites)	41.9	1.72	33.0	1.67

material. This result is likely due to the relatively small length and aspect ratio of the as-received Thermocarb Specialty Graphite. The as-received synthetic graphite has a mean length of 68 microns 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 65 microns (aspect ratio = 1.65). In the nylon-based composites containing both carbon fibers and synthetic graphite, the mean length of the synthetic graphite was 51 microns (aspect ratio = 1.78). The results for the polycarbonate-based composites were similar to those of the nylon composites, with the length decreasing to 46.2 microns (aspect ratio = 1.68) in the 30 wt % formulation, and to a 33 micron length (aspect ratio = 1.67) 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 angle of thermal conductivity measurement. In the case of the in-plane thermal conductivity samples, it is desirable to have the fillers oriented in the direction of polymer flow that occurs during injection molding, which is the same as the direction of measurement. For these measurements, all of the angles will be between zero and 90°.

Figure 6 shows the orientation results for the in-plane thermal conductivity samples containing only 40 wt % Thermocarb Specialty Graphite or 40 wt % carbon fiber in both polymers. An angle of zero de-

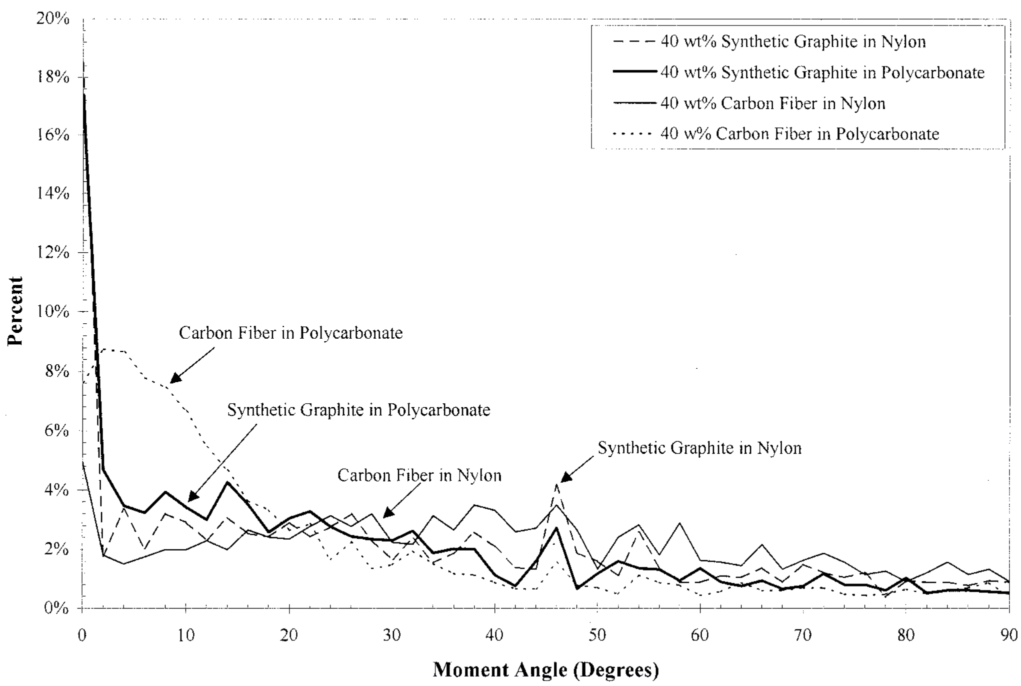

Figure 6 In-plane thermal conductivity specimens filler orientation results.

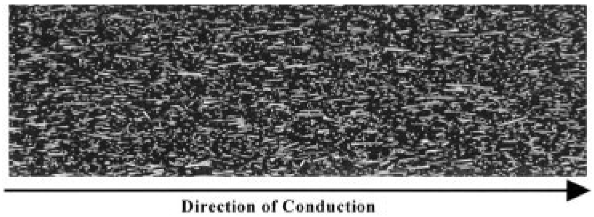

Figure 7 Forty weight percent carbon fiber in polycarbonate in-plane thermal conductivity sample at 200× magnification.

grees signifies that the particles/fibers are aligned in the direction of flow into the mold, which is also the direction of conductivity measurement for the in-plane samples. An angle of 90° means that a filler is perpendicular to the direction of flow/measurement. The results in Figure 6 indicate that the fillers are primarily oriented in the same direction as the thermal conductivity measurement (more fillers found close to 0° orientation angle). This orientation is also evident in Figures 7 and 8. The arrow below Figures 7 and 8 indicates the thermal conductivity measurement direction. For the in-plane thermal conductivity sample containing 40 wt % carbon fiber in polycarbonate (Fig. 7), the mean orientation angle was 18° with a median of 10°, and a standard deviation of 21° (7953 fibers measured). For the in-plane conductivity sample containing 40 wt % synthetic graphite in polycarbonate (Fig. 8), the mean orientation angle was 27° with a median of 22°, and a standard deviation of 25° (6476 particles measured). These orientation results indicate that the carbon fiber is aligned slightly more in the direction of thermal conductivity measurement (mean of 18° for carbon fiber compared to 27° for synthetic graphite particles). This result likely due to the higher aspect ratio of the carbon fiber (approximately 8) compared to approximately 1.7 for the synthetic graphite particles in the composite samples. The results shown in Figures 6, 7, and 8 are typical for all of the carbon-filled composites studied in this project. Additionally, these results agree with those of other researchers who obtained similar distribution of orientation angles.[25–27]

Figure 9 shows the orientation results for several through-plane thermal conductivity samples. In this case, the orientation angle is closer to 90°, indicating that the fibers/particles are primarily orientated transverse to the thermal conductivity measurement direction. Figure 10 displays an image of the through-plane thermal conductivity sample containing 20 wt % Thermocarb Specialty Graphite in polycarbonate. For this image, the mean orientation angle was 66° with a median of 73°, and a standard deviation of 22° (1788 particles measured). The line below Figure 10 indicates the direction of thermal conductivity measurement. Figures 9 and 10 are typical of all of the carbon filled composites studied in this project.

Through-plane thermal conductivity results

The through-plane thermal conductivity results for the composites containing only varying amounts of carbon black in both polymers is shown in Figure 11. Each data point shown in Figure 11 is the mean of four samples tested per formulation. The standard deviation was less than 2% of the mean. Figure 11 shows that adding carbon black to both resins causes the thermal conductivity to increase slightly. Because nylon is a semicrystalline polymer, the thermal conductivity of the nylon based resins is higher than that of the polycarbonate based resins. For nylon, the thermal conductivity increases from 0.30 W/mK for the pure nylon to 0.45 W/mK for the composites containing 10 wt % (6.6 vol %) carbon black. For polycarbonate, the thermal conductivity increases from 0.23 W/mK for the pure polymer to 0.33 W/mK for the composites containing 10 wt % (6.9 vol%) carbon black. As stated previously, carbon black was not expected to cause a large increase in composite thermal conductivity.

The through-plane thermal conductivity results for the composites containing only varying amounts of Thermocarb Specialty Graphite, which is a high-purity synthetic graphite, in both polymers is shown in Figure 12. Each data point shown in Figure 12 is the mean of four to seven samples tested per formulation. The standard deviation was typically less than 5% of the mean. Figure 12 shows that adding synthetic graphite to both resins causes the thermal conductivity to increase dramatically. For nylon, the thermal conductivity increases from 0.30 W/mK for the pure nylon to 1.1 W/mK for the composites containing 40 wt % (25.3 vol %) synthetic graphite. For polycarbonate, the thermal conductivity increases from 0.23 W/mK for the pure polymer to 1.0 W/mK for the composites containing 40 wt % (26.3 vol %) synthetic graphite.

The through-plane thermal conductivity results for the composites containing only varying amounts of carbon fiber in both polymers is shown in Figure 13. Each data point shown in Figure 13 is the mean of four to six samples tested per formulation. The standard deviation was typically less than 5% of the mean. Figure 13 shows that adding carbon fiber to both resins also causes the thermal conductivity to increase dramatically. For nylon, the thermal conductivity in-

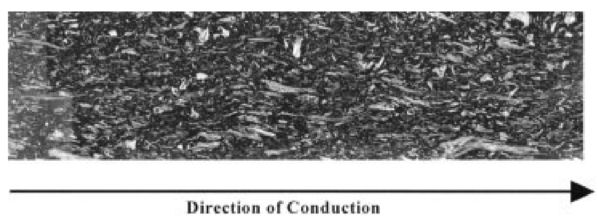

Figure 8 Forty weight percent Thermocarb specialty graphite in polycarbonate in-plane thermal conductivity sample at 200× magnification.

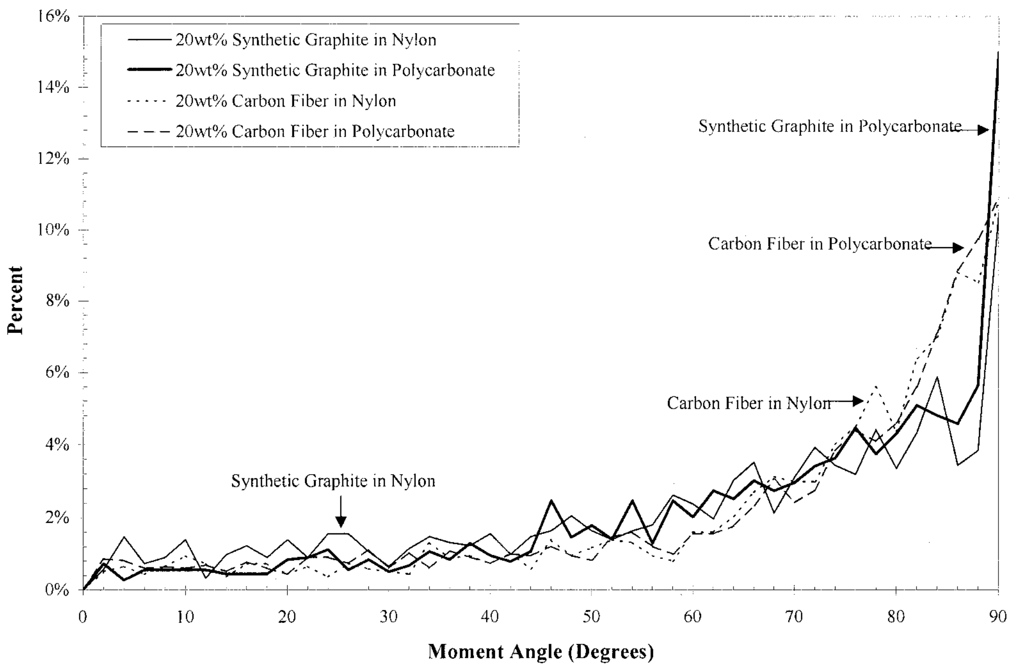

Figure 9 Through-plane thermal conductivity specimens filler orientation results.

creases from 0.30 W/mK for the pure nylon to 0.95 W/mK for the composites containing 40 wt % (26.1 vol %) carbon fiber. For polycarbonate, the thermal conductivity increases from 0.23 W/mK for the pure polymer to 0.74 W/mK for the composites containing 40 wt % (27.1 vol %) carbon fiber.

Table IV shows the mean through-plane thermal conductivity results for each factorial design formulation for the nylon based resins. Table V gives the through-plane thermal conductivity results for each factorial design formulation for the polycarbonate based resins. A complete replicate of the full factorial was completed in each resin. Hence, there is a column labeled "Original" and "Replicate." These columns show the mean, standard deviation, and number of through-plane thermal conductivity samples tested. As stated previously, Table I defines the factorial design formulations in both polymers.

The results in Tables IV and V show a wide range of values for the different filler combinations. For example, the composite containing all three fillers in nylon had a thermal conductivity of 2.0 W/mK, which is higher than the resin containing 40 wt % Thermocarb Specialty Graphite (1.1 W/mK). Although it is apparent that the combinations of fillers produces higher conductivity results, the exact effect of the combinations is not obvious without the application of statistical experimental design calculations.

Factorial design analysis: through-plane thermal conductivity

Using the results shown in Tables IV and V, an analysis of the factorial design was completed. This was performed using the Minitab version 13 Statistical Software package. Calculations were also performed using Microsoft Excel 2000 to verify and understand the results obtained with the Minitab calculations. For

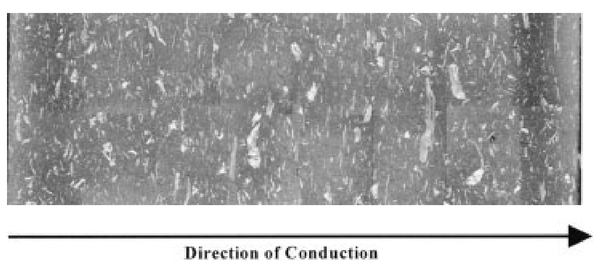

Figure 10 Twenty weight percent Thermocarb specialty graphite in polycarbonate through-plane thermal conductivity sample at 200× magnification.

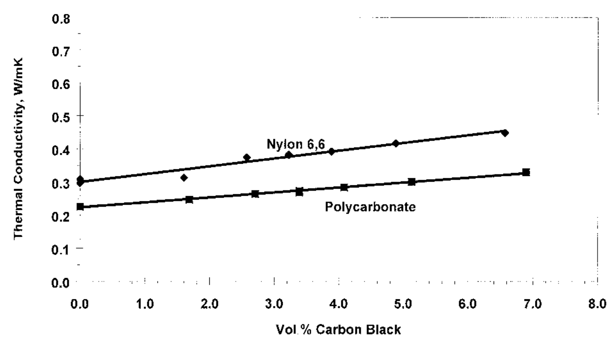

Figure 11 Through-plane thermal conductivity of composites containing only carbon black.

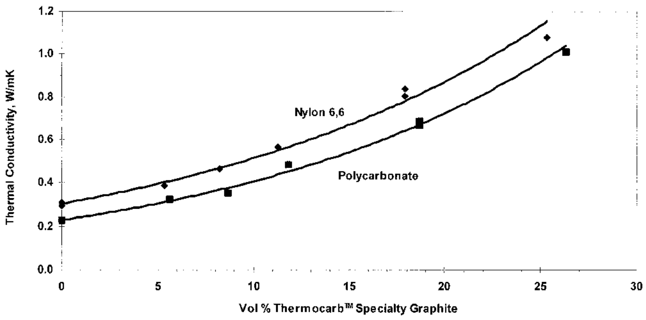

Figure 12 Through-plane thermal conductivity of composites containing only Thermocarb specialty graphite.

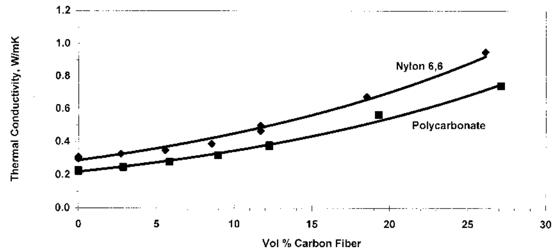

Figure 13 Through-plane thermal conductivity of composites containing only carbon fiber.

this analysis, the effects, coefficients, and T and P values for the through-plane thermal conductivity results were calculated. For all statistical calculations, the 95% confidence level was used.

Factorial designs were used in the project because they are the most efficient type of experiment to determine the effect of each filler and any possible interactions between fillers. Factorial design experiments are more efficient than performing one-factor-at-a-time experiments. The total number of experiments that must be run to determine the effects of the factors can be significantly reduced by examining multiple factors at one time. By using factorials, one can determine the effect that each factor (filler) has on the system by calculating a single value to quantify the increase in conductivity as the weight percent of a filler is increased. These calculated effects can then be ranked to determine which fillers and combinations of fillers produced a larger change in the thermal conductivity values. In addition, the use of factorial designs can prevent the misinterpretation of data that can occur when interaction effects are present in an experiment.

The effects, coefficients, and T and P values for the nylon 6,6 based composites are given in Table VI, showing the values for all of the filler combinations. Further investigation of Table VI yields some important information regarding the effects that fillers have on conductivity. First, all the effect terms are positive, which indicates that the addition of any filler increases the thermal conductivity of the composite. Second, the effect term is the largest for the synthetic graphite (Thermocarb Specialty Graphite), which indicates that synthetic graphite causes the largest increase in composite through-plane thermal conductivity. After synthetic graphite the effect of the fillers follows the following order: carbon fiber, the combination of synthetic graphite and carbon fiber, carbon black, and last, the combination of synthetic graphite and carbon black. The six formulations mentioned previously in this paragraph are all statistically significant at the 95% confidence level ($p < 0.05$). Two formulations, the carbon black/carbon fiber combination and the three filler combination, are not statistically significant ($p > 0.05$).

Table VII shows the results of the factorial design analysis for the polycarbonate based composites. In this case, the order of the effects is as follows : synthetic graphite, carbon fiber, synthetic graphite/carbon fiber combination, carbon black, synthetic graphite/carbon black combination, and last, the carbon black/carbon fiber combination. Once again, the fillers that cause the largest increase in composite through-plane thermal conductivity is synthetic graphite, then carbon fiber, and then the synthetic graphite/carbon fiber combination. The seven formulations mentioned previously in this paragraph are all statistically significant at the 95% confidence level ($p < 0.05$). Only one formulation, the carbon black/synthetic graphite/carbon fiber combination is not statistically significant ($p > 0.05$).

TABLE IV
Through-Plane Thermal Conductivity Results for Factorial Design Formulations in Nylon 6,6

Formulation	Thermal conductivity, W/mK Original	Thermal conductivity, W/mK Replicate	Thermal conductivity, W/mK mean
No filler	0.297 ± 0.007 $n = 4$	0.309 ± 0.006 $n = 4$	0.303
CB	0.381 ± 0.003 $n = 4$	0.383 ± 0.002 $n = 4$	0.382
SG	0.802 ± 0.050 $n = 6$	0.836 ± 0.062 $n = 6$	0.819
CB*SG	0.956 ± 0.003 $n = 4$	0.999 ± 0.072 $n = 6$	0.978
CF	0.464 ± 0.021 $n = 4$	0.498 ± 0.020 $n = 4$	0.481
CB*CF	0.556 ± 0.039 $n = 4$	0.578 ± 0.035 $n = 4$	0.567
SG*CF	1.733 ± 0.060 $n = 5$	1.773 ± 0.022 $n = 4$	1.753
CB*SG*CF	1.993 ± 0.074 $n = 4$	1.963 ± 0.096 $n = 5$	1.978

TABLE V
Through-Plane Thermal Conductivity Results for Factorial Design Formulations in Polycarbonate

Formulation	Thermal conductivity, W/mK Original	Thermal conductivity, W/mK Replicate	Thermal conductivity, W/mK mean
No filler	0.226 ± 0.002 n = 4	0.226 ± 0.001 n = 4	0.226
CB	0.273 ± 0.003 n = 4	0.269 ± 0.005 n = 4	0.271
SG	0.666 ± 0.009 n = 4	0.687 ± 0.015 n = 4	0.677
CB*SG	0.786 ± 0.023 n = 4	0.802 ± 0.008 n = 4	0.794
CF	0.372 ± 0.006 n = 4	0.378 ± 0.004 n = 4	0.375
CB*CF	0.486 ± 0.011 n = 4	0.497 ± 0.002 n = 4	0.492
SG*CF	1.551 ± 0.039 n = 4	1.570 ± 0.080 n = 4	1.561
CB*SG*CF	1.866 ± 0.100 n = 6	2.109 ± 0.030 n = 4	1.988

In-plane thermal conductivity results

Due to the time consuming nature of this test, in-plane thermal conductivity tests were only conducted on the more thermally conductive samples. Tables VIII and IX list these results for both the nylon and polycarbonate based formulations. These tables include the mean, standard deviation, and number of samples tested. The last column in both of these tables shows the mean in-plane thermal conductivity/mean through-plane thermal conductivity.

When looking at the samples containing only synthetic graphite, several observations can be made. For both the nylon 6,6 and polycarbonate-based samples with 30 wt % synthetic graphite, the in-plane thermal conductivity is approximately 4 W/mK, which is approximately five times higher than the through-plane thermal conductivity for these materials. At 40 wt % Thermocarb Specialty Graphite in both polymers, the in-plane thermal conductivity increases further to approximately 8 W/mK, which corresponds to a thermal conductivity anisotropy ratio (in-plane thermal conductivity/through-plane thermal conductivity) of about 8. These higher values for in-plane thermal conductivity are likely due to the fact that the direction of heat measurement is the same as the direction of the synthetic graphite particles.

For the resins containing only carbon fiber, the in-plane thermal conductivity is even higher. Again, this is likely due to the fact fibers are aligned in the direction of thermal conductivity measurement and that the aspect ratio of the carbon fiber is approximately 8 compared to approximately 1.7 for Thermocarb. Higher filler aspect ratio in the direction of heat measurement has been shown to increase the thermal conductivity of the composite.[9,28] For 20 wt % carbon fiber in both polymers, the in-plane thermal conductivity is approximately 5 W/mK, with an anisotropy ratio of about 12. For 30 wt % carbon fiber in both polymers, the in-plane thermal conductivity increases to approximately 9 W/mK, which corresponds to an anisotropy ratio of about 15. For 40 wt % carbon fiber in both polymers, the in-plane thermal conductivity increases even further to approximately 14 W/mK, which corresponds to an anisotropy ratio of about 17.

When viewing the results for the composites containing more than one type of conductive filler, several observations can be made. First, the anisotropy ratio of the samples containing 5 wt % carbon black and 30 wt % Thermocarb in both polymers is approximately 6. Second, the anisotropy ratio of the samples containing the other three mixtures of fillers in both polymers is about 9.

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

TABLE VI
Factorial Design Analysis for Nylon 6,6-Based Conductive Resins

Term	Effect	Coefficient	T	*P*
Constant		0.908	170.0	0.000
CB	**0.137**	**0.069**	**12.9**	**0.000**
SG	**0.949**	**0.474**	**88.9**	**0.000**
CF	**0.574**	**0.287**	**53.8**	**0.000**
CB*SG	**0.055**	**0.027**	**5.1**	**0.001**
CB*CF	0.018	0.009	1.7	0.123
SG*CF	**0.393**	**0.196**	**36.8**	**0.000**
CB*SG*CF	0.015	0.007	1.4	0.201

TABLE VII
Factorial Design Analysis for Polycarbonate-Based Conductive Resins

Term	Effect	Coefficient	T	P
Constant		0.798	52.0	0.000
CB	**0.177**	**0.088**	**5.8**	**0.000**
SG	**0.914**	**0.457**	**29.8**	**0.000**
CF	**0.612**	**0.306**	**19.9**	**0.000**
CB*SG	**0.096**	**0.048**	**3.1**	**0.014**
CB*CF	**0.095**	**0.048**	**3.1**	**0.015**
SG*CF	**0.427**	**0.214**	**13.9**	**0.000**
CB*SG*CF	0.060	0.030	1.9	0.089

TABLE VIII
In-Plane Thermal Conductivity Results for Selected Nylon Based Formulations

Formulation	In-plane thermal cond., W/mK	Thru-plane thermal cond., W/mK	In-plane/thru plane thermal cond.
Synthetic graphite only			
30 wt %	4.1 ± 0.5 n = 4	0.82 ± 0.06 n = 12	5.0
40 wt %	8.2 ± 2.8 n = 3	1.08 ± 0.10 n = 7	7.6
Carbon fiber only			
20 wt %	5.8 ± 0.7 n = 3	0.48 ± 0.03 n = 8	12.1
30 wt %	10.0 ± 0.5 n = 3	0.68 ± 0.04 n = 4	14.7
40 wt %	16.6 ± 1.3 n = 2	0.95 ± 0.11 n = 6	17.5
CB/SG combination	6.2 ± 0.9 n = 4	0.98 ± 0.06 n = 10	6.3
CB/CF combination	7.9 ± 0.4 n = 4	0.57 ± 0.04 n = 8	13.9
SG/CF combination	15.0 ± 1.1 n = 3	1.75 ± 0.05 n = 9	8.6
CB/SG/CF combination	15.8 ± 1.3 n = 3	1.98 ± 0.08 n = 9	8.0

original length (168 microns) and aspect ratio (16.8). However, the length (typically 60 to 70 microns) and aspect ratio (typically 1.7 to 1.8) of the Thermocarb Specialty Graphite in the composite specimens remain similar to that of the as received material. This high-purity synthetic graphite likely maintained its size better compared to carbon fiber since the as-received Thermocarb material has a smaller length and aspect ratio. Concerning orientation, for the through-plane thermal conductivity samples, the synthetic graphite particles and carbon fibers are mainly oriented transverse to the direction of thermal conductivity measurement. For the in-plane thermal conductivity samples, the synthetic graphite particles and carbon fibers are mainly oriented in the direction of thermal conductivity measurement. Hence, for the same formulation, the in-plane composite thermal conductivity is higher than the through-plane thermal conductivity. For example, in both polymers for the samples containing only Thermocarb, the anisotropy ratio is approximately 5 for the 30 wt % case and 8 for the 40 wt % case. When carbon fibers are used in a composite, the anisotropy ratio is even higher. For 20, 30, and 40 wt % carbon fiber in both polymers, the anisotropy ratio is approximately 12, 15, and 17, respectively. The higher in-plane thermal conductivity for the composites containing carbon fiber is likely due to the higher aspect ratio of about 8 for the carbon fiber compared to approximately 1.7 for the Thermocarb.

Considering only the through-plane thermal conductivity of composites containing a varying amount of a single filler, Thermocarb caused the largest increase in composite through-plane thermal conductivity. For nylon, the thermal conductivity increased from 0.3 W/mK (pure polymer) to 1.1 W/mK for the composites containing 40 wt % Thermocarb. Carbon fiber had the second largest effect on through-plane thermal conductivity. For nylon, the thermal conductivity increased again from 0.3 W/mK (pure polymer) to 1.0 W/mK for 40 wt % carbon fiber composites. Carbon black had the least effect on through-plane thermal conductivity.

By studying the though-plane thermal conductivity factorial experiment results in both nylon and polycarbonate, the fillers can be ranked in the following order shown below:

$$\text{Thermocarb} > \text{Carbon Fiber} > \text{Thermocarb/Carbon Fiber Combination.}$$

TABLE IX
In-Plane Thermal Conductivity Results for Selected Polycarbonate-Based Formulations

Formulation	In-plane thermal cond., W/mK	Thru-plane thermal cond., W/mK	In-plane/thru plane thermal cond.
Synthetic graphite only			
30 wt %	3.7 ± 0.5 n = 5	0.68 ± 0.02 n = 8	5.4
40 wt %	8.9 ± 2.8 n = 4	1.01 ± 0.03 n = 4	8.9
Carbon fiber only			
20 wt %	4.7 ± 0.1 n = 3	0.38 ± 0.01 n = 8	12.4
30 wt %	8.7 ± 0.9 n = 2	0.57 ± 0.04 n = 5	15.3
40 wt %	12.2 ± 1.2 n = 2	0.74 ± 0.03 n = 6	16.5
CB/SG combination	4.5 ± 0.3 n = 4	0.79 ± 0.02 n = 8	5.7
CB/CF combination	4.6 ± 0.2 n = 4	0.49 ± 0.01 n = 8	9.4
SG/CF combination	13.9 ± 1.3 n = 4	1.56 ± 0.06 n = 8	8.9
CB/SG/CF combination	20.1 ± 3.4 n = 2	1.99 ± 0.15 n = 10	10.1

Hence, Thermocarb caused the largest increase in composite through-plane thermal conductivity. Another important result is that the Thermocarb/carbon fiber combination causes a statistically significant increase in composite thermal conductivity. To the authors' knowledge, this is the first time in the literature that a synergistic effect of combining different carbon fillers on composite thermal conductivity has been observed. It is likely that thermally conductive pathways are formed that "link" the carbon fiber with the synthetic graphite.

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