Tensile and Impact Properties of Carbon Filled Nylon-6,6 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, ultimate tensile stress, strain at ultimate tensile stress, and notched Izod impact strength are also important and cannot be ignored. This study focused on performing compounding runs, followed by injection molding and evaluation of tensile and impact properties of carbon filled nylon-6,6 based resins. The three carbon fillers investigated include an electrically conductive carbon black, synthetic graphite particles, and a surface treated polyacrylonitrile (PAN) based carbon fiber. Resins containing varying amounts of these single carbon fillers were produced and tested. In addition, combinations of fillers were investigated by conducting a full 2^3 factorial design and a complete replicate. The addition of carbon fiber increased the composite tensile modulus, ultimate tensile stress, and impact strength. Also, in many cases, combining two or three different fillers caused a statistically significant effect at a 95% confidence level. When comparing the results of this study with prior work, it appears that increased heteroatoms present on the carbon fiber surface likely improve composite ultimate tensile stress and impact strength. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2881–2893, 2004

Key words: strength; fillers; nylon; impact resistance

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) include 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, semi-conducting (e.g., fuel gages, etc.), or Electromagnetic Interference/Radio Frequency Interference (EMI/RFI) 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 and coworkers studied the electrical conductivity of carbon fiber reinforced polypropylene/polyaniline complex blends.[11] 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. investigated the electrical conductivity and mechanical properties of composites containing both graphite and carbon fiber in high density polyethylene and ultra-high molecular weight polyethylene.[12] 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, ultimate tensile stress, strain at ultimate tensile stress, and notched Izod impact strength are also important and cannot be ignored. A conductive resin must possess reasonable mechanical properties in order to be used.

In this study, we performed compounding runs followed by injection molding and tensile and impact testing of carbon filled nylon-6,6 resins. The three carbon fillers investigated include an electrically conductive carbon black, synthetic graphite particles, and a surface treated polyacrylonitrile (PAN) based carbon fiber. Fifteen 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. The goal of this research was to determine the effects of each filler and combinations of different fillers on the tensile and impact properties of the resins.

EXPERIMENTAL

Materials

The matrix used was DuPont Zytel 101 NC010, an unmodified semicrystalline nylon-6,6 polymer. The

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TABLE I
Properties of Akzo Nobel Fortafil 243 PAN Based 3.2 mm Chopped and Pelletized Carbon Fiber[18]

Carbon content	95 wt %
Electrical resistivity	0.00167 ohm-cm
Thermal conductivity	20. W/mK (axial direction)
Tensile strength	3800 MPa
Tensile modulus	227 GPa
Specific gravity	1.74 g/cc
Fiber diameter	7.3 μm
Fiber shape	Round
Fiber mean length	3.2 mm (entire range is 2.3 mm to 4.1 mm)
Binder content[a]	2.6 wt %
Bulk density	356 g/L

[a] A propietary polymer that adheres pellets together and promotes adhesion with nylon matrix.

properties of this polymer are discussed elsewhere.[13,15] Three different carbon fillers were employed in this project. Akzo Nobel Ketjenblack EC-600 JD, an electrically conductive carbon black, was used. The highly branched, high surface area carbon black structure allows it to have contact with a large amount of polymer, which results in improved electrical conductivity at low carbon black concentrations. Thermocarb™ TC-300 Specialty Graphite, a high quality synthetic graphite that is available from Conoco, Inc., was used due to its high thermal conductivity and moderately high electrical conductivity. The properties of these two fillers are discussed elsewhere.[13,16,17] Akzo Nobel's Fortafil 243 PAN based 3.2 mm chopped and pelletized carbon fiber was used to improve the electrical and thermal conductivity and the tensile strength of the resin. Fortafil 243 was surface treated and then formed into pellets. A proprietary polymer (sizing) was used as a binder for the pellets that also promotes adhesion with nylon. Table I shows the properties of this carbon fiber.[18]

In this study, a 2^3 factorial design (three factors or fillers in this case at two different loading levels) was utilized, and a complete replicate was completed. 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 Fortafil 243. Table II shows the factorial design formulations. In Table II, "CB" signifies carbon black, "SG" signifies synthetic graphite (Thermocarb™ TC-300 Specialty Graphite), and "CF" signifies carbon fiber. Since this project focused on producing highly conductive composites, the high loading levels were chosen to ensure that the filler amounts would be above the electrical conductivity percolation threshold. Another consideration was that the total weight percent of filler for the composite with all fillers at the high levels be limited to 55 wt %. Higher filler amounts would likely make it difficult to extrude and injection mold the conductive resin into test specimens.

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

Test specimen fabrication

For this entire project, the fillers were used as received. Zytel 101 NC010 was 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 co-rotating intermeshing twin screw with 10 zones and a length/diameter ratio of 40. The screw design was chosen to obtain the maximum possible conductivity and is described in detail elsewhere.[19] Our goal was to minimize filler degradation while still dispersing the fillers well in the polymer. The same screw design was used for the entire project. The Zytel polymer pellets 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

TABLE II
Filler Loadings in Factorial Design Formulations for Nylon-6,6

Formulation	Ketjenblack EC-600 JD (wt%)	Thermocarb™ TC-300 specialty graphite (wt %)	Fortafil 243 (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

accurately control the amount of each material added to the extruder.

After passing through the extruder, the polymer strands (3 mm in diameter) were placed in a water bath and then a pelletizer that produced nominally 3 mm long pellets. After compounding, the pelletized composite resin was dried again and then stored in moisture barrier bags prior to injection molding.

A Niigata injection molding machine, model $NE85UA_4$, was used to produce the test specimens. It had 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 were 396 mm, 180 mm, and 144 mm, respectively.

A four-cavity mold was used to produce 3.2 mm thick ASTM Type I tensile bars (end gated) and 3.2 mm thick rectangular bars (12.6 cm long by 12.7 mm wide, end gated). The tensile and impact properties of all formulations were determined.

Tensile test method

The tensile properties (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). For each formulation, at least 5 samples were tested.

Izod impact test method

Notched Izod impact tests were conducted under ambient conditions for all formulations using ASTM D256-97.[21] One injection molded, 3.2 mm thick rectangular bar was cut into two rectangular Izod samples (3.2 mm thick by 12.7 mm wide by 62 mm long). Then the samples were notched (45°) using a CS-93E Sample Notcher. A CEAST RESIL 25 Izod Impact Tester was used. The nylon-6,6 based samples were all tested DAM. For each formulation, typically 15 samples were tested.

TABLE III
Single Filler Loading Levels for Nylon-6,6

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
Fortafil 243 carbon fiber	5.0, 7.0, 10.0, 15.0, 20.0, 30.0, 40.0

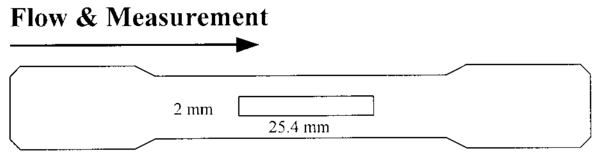

Figure 1 Portion of tensile bar from which orientation specimens were cut.

Filler length and aspect ratio test method

In order 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. 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 were measured. For each formulation, between 300 and 1100 particles/fibers were measured. Due to the extremely small size of the carbon black (primary aggregates are 30 to 100 nm), the length and aspect ratio of the carbon black were not measured.

Filler orientation test method

In order 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, the orientation of only the synthetic graphite particles and carbon fibers were determined. One 25 mm by 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.

Surface energy test method

Surface energies for the three fillers were measured using the Washburn adsorption method.[22] The two components of the total surface energy, a polar and a dispersive component, were determined.[23] This analysis was performed using a Kruss Processor Tensiometer K12 with an FL12 powder cell accessory, and was done by Kruss Laboratory Services and Augustine Scientific personnel.[24-25] The total, polar, and dispersive components of the polymer surface energy were determined in the melt phase (to simulate extrusion and injection molding; 270°C for nylon-6,6) using the pendant drop technique by Kruss Laboratory Services.[24] A Kruss Drop Shape Analysis System DSA10 was used.

X-Ray photoelectric spectroscopy

X-ray Photoelectric Spectroscopy (XPS) was used in order to determine the surface composition of the various carbon fillers. Since each element has a unique set of binding energies, XPS can determine the elements present in the top 50–100 angstroms of the sample surface. A Perkin-Elmer PHI 1600 XPS system was used in an ultra-high vacuum chamber. The Thermocarb™ TC-300 Specialty Graphite and the Ketjenblack EC-600 JD samples were pressed into 13 mm diameter wafers using a hydraulic press. The Fortafil 243 carbon fiber was mounted on the sample holder.[26]

Environmental scanning electron microscopy

A Philips XL-40 Environmental Scanning Electron Microscope (ESEM) was used to view the tensile fracture surfaces of selected samples. This was done to determine whether it was possible to view any differences in filler-matrix adhesion.

Nanoscratch testing

An MTS Nano Indenter XP was used for the scratch tests on the end view (2 mm wide by 3 mm thick face) of orientation samples cut from the tensile bars (see Fig. 1). This instrument performs scratch tests using a Berkovich indenter with a submicron radius. This test system can resolve the indentation depth to less than 0.01 nm, and the indentation load is measured to a precision of 50 nN. The tests were performed under a constant normal load of 40 mN, and the scratch length was 500 μm. The scratch velocity was 10 μm/s. In a typical test, the penetration depth of the scratch tip, the normal force applied on the sample, and the friction force developed between the sample and the scratch tip were recorded. The scratch tests were performed to determine whether they could provide a measure of filler–matrix adhesion.

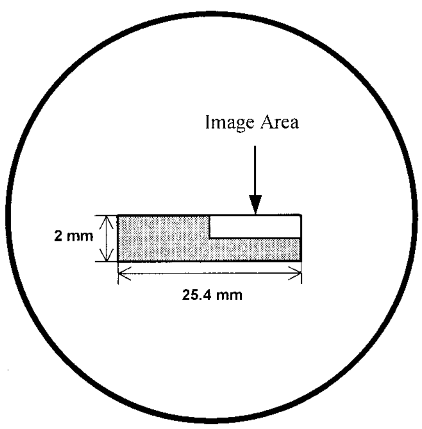

Figure 2 Sample arrangement for filler orientation analysis.

TABLE IV
Mean Length and Aspect Ratio Results for Factorial Design Formulations[26–28]

Formulation	Nylon-6,6 Length (μm)	Nylon-6,6 Aspect ratio
As received carbon fibers (CF)	3,200	438.36
As received Thermocarb™ (SG)	68.3	1.80
SG only composites	70.6	1.68
SG only replicate composites	68.5	1.70
CF only composites	120.7	16.54
CF only replicate composites	113.5	15.55
CF (SG + CF composites)	110.5	15.14
SG (SG + CF composites)	44.2	1.70
CF (SG + CF replicate composites)	106.2	14.55
SG (SG + CF replicate composites)	53.0	1.66

RESULTS AND DISCUSSION

Filler length and aspect ratio results

Table IV shows the mean length and aspect ratio (length/diameter) results of the synthetic graphite particles and carbon fibers for the factorial design formulations 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.[26–28]

The results in Table IV show that there is significant degradation of the carbon fibers following the extrusion and injection molding steps. Prior to processing, the mean length of the carbon fibers was 3,200 μm with an aspect ratio (length/diameter) of 438. After processing, in the 20 wt % carbon fiber formulation in nylon-6,6, the fibers had a mean length of 117 μm (aspect ratio = 16.0). In the nylon based composites containing both carbon fibers and synthetic graphite, the mean length of the fibers was 108 μm (aspect ratio = 14.8). These length results are comparable to those reported by Bigg, which showed that carbon fiber/nylon-6,6 composites had fiber lengths of approximately 130 μm after extrusion and injection molding.[29]

Table IV shows that the length and aspect ratio of the synthetic graphite particles in the composite specimens remain similar to those of the as received material. This result is likely due to the relatively small

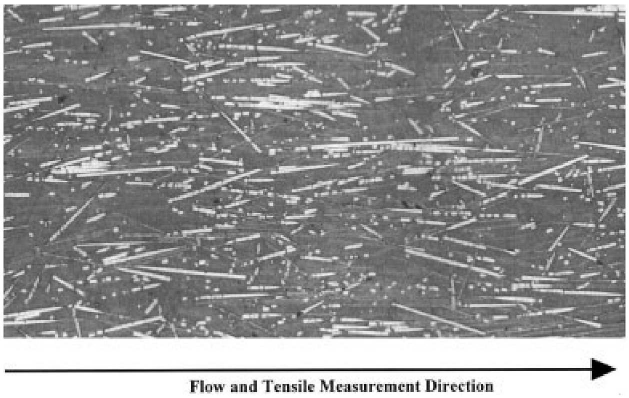

Figure 3 Photomicrograph of a 20 wt % Fortafil 243 carbon fiber in nylon-6,6 tensile specimen at a magnification of 200×.

length and aspect ratio of the as received Thermocarb™ TC-300 Specialty Graphite. The as received synthetic graphite had 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 had a mean length of 70 μm (aspect ratio = 1.69) after processing. In the nylon based composites containing both carbon fibers and synthetic graphite particles, the mean length of the synthetic graphite was 49 μm (aspect ratio = 1.68).

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 end gated tensile test specimen mold. For these measurements, all of the angles were between 0 and 90°. An angle of 0° degrees 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 and to the longitudinal tensile test direction.

For the tensile specimen containing 30 wt % Thermocarb™ TC-300 Specialty Graphite, the mean orientation angle was 28° with a standard deviation of 23° (769 particles measured). A photomicrograph of this sample is shown elsewhere.[30] The mean orientation angle varied from 28° to 31° for all composites containing Thermocarb™ TC-300 Specialty Graphite. Figure 3 shows a photomicrograph of a tensile sample containing 20 wt % Fortafil 243 carbon fiber in nylon-6,6. The arrow under this figure indicates the tensile measurement direction, which is also the direction of flow into the mold. For this sample, the mean orientation angle was 24° with a standard deviation of 23° (2511 fibers measured). The mean orientation angle varied from 15° to 28° for all the composites containing Fortafil 243. Hence, the orientation angle is closer to 0°, indicating that the fibers/particles are primarily oriented in the longitudinal tensile test direction. Additionally, these results agree with those of other researchers who obtained similar distributions of orientation angles.[31–34]

Surface energy and XPS results

Table V displays the polar and dispersive surface energy components for all of the materials used.[24-25] The total surface energy for the pure nylon-6,6 was measured to be 45.92 mJ/m^2 in the melt phase. The total surface energy values for the carbon black, synthetic graphite particles and carbon fibers were 21.77 mJ/m^2, 24.00 mJ/m^2, and 28.89 mJ/m^2, respectively. The surface polarity values (polar surface energy component/total surface energy) are also given in Table V.[24-25] Because the Fortafil carbon fiber was surface treated, its surface polarity value was the highest of the three fillers used.

Results from the XPS analysis for all three fillers used are also shown in Table V.[26] The carbon black and synthetic graphite particles only had two elements present on the filler surface, carbon and oxygen. The Fortafil carbon fiber had carbon (86.6%), oxygen (8.5%), nitrogen (1.5%) and sodium (3.4%) present. This table shows that, as expected, as the amount of heteroatoms present on the filler surface increased, the polar component of the surface energy increased.

TABLE V
Surface Energy and XPS Results[24–26]

Material	Polar component (mJ/m^2)	Dispersive component (mJ/m^2)	Total surface energy (mJ/m^2)	Surface polarity (%)	Oxygen on filler surface (Atomic %)
Zytel 101 NC010	17.24	28.68	45.92	37.5	—
Carbon black	2.18	19.59	21.77	10.0	1.3
Synthetic graphite particles	3.99	20.01	24.00	16.6	1.8
Forafil carbon fiber	8.71	20.18	28.89	30.1	8.5

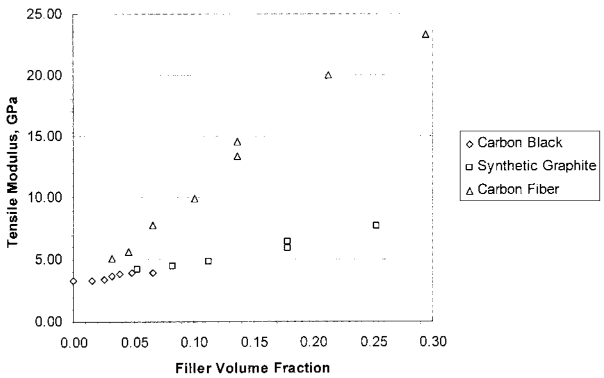

Figure 4 Tensile modulus of single filler composites.

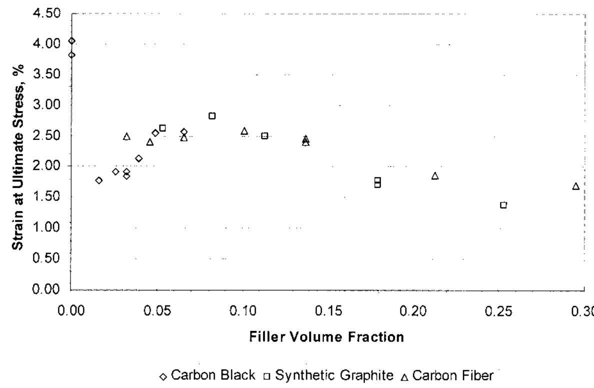

Figure 6 Strain at ultimate tensile stress of single filler composites.

Tensile results

Figures 4–6 show the tensile results for composites containing varying amounts of single fillers in volume fractions. These formulations correspond to those shown in Table III, which displays weight percents. For comparison purposes, the tensile modulus of the neat nylon-6,6 was 3.10 GPa according to the vendor literature.[15] The ultimate tensile strength of the neat nylon-6,6 was 83 MPa according to the vendor literature.[15] The aspect ratio (length/diameter) of the fillers in the composite test specimens was 1.0 for carbon black,[35] 1.68 for synthetic graphite, and 16 for carbon fibers.

The tensile modulus results for composites filled only with varying amounts of the single fillers in nylon-6,6 are located in Figure 4. Several observations can be made from Figure 4. First, for the neat nylon-6,6 the experimental tensile modulus (3.28 and 3.30 GPa) agrees well with the vendor literature (3.10 GPa). Second, since the tensile modulus of each filler is higher than that of the matrix, adding filler increases the composite tensile modulus. Third, since the aspect ratio of the carbon fibers in the composite test sample is the largest, at approximately 16, the modulus increases most for the samples containing carbon fibers.

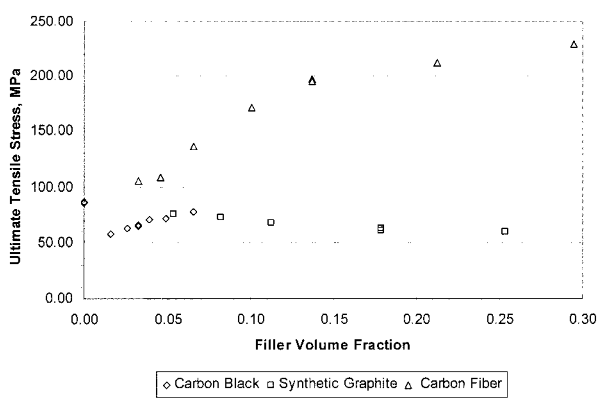

Figure 5 Ultimate tensile stress of single filler composites.

Figure 5 illustrates the ultimate tensile stress results for composites filled only with varying amounts of the single fillers in nylon-6,6. For the neat nylon-6,6, the experimental ultimate tensile strength values (85.2 and 86.7 MPa) agree well with the vendor literature (83.0 MPa). As expected, due to the length (117 μm) of the carbon fibers, adding carbon fibers significantly increases the composite ultimate tensile stress. Another expected result was that, due to the lower length (70 μm) of the synthetic graphite, the composite ultimate tensile stress decreased when synthetic graphite was added. When carbon black was added to the composite, the ultimate tensile stress increased. This result was not expected due to the short length (primary aggregates are 30 to 100 nm) of the carbon black. These unusual results for carbon black have been reported elsewhere for carbon black in ethylene vinyl acetate.[36]

Figure 6 illustrates the strain at ultimate tensile stress results for composites filled only with varying amounts of the single fillers in nylon-6,6. For the single fillers, the strain at ultimate tensile stress results follow the same trends as the ultimate tensile stress. As expected, adding any filler causes the composite strain to decrease.

Notched Izod impact strength results

Figure 7 shows the notched Izod impact strength results for composites containing varying amounts of single fillers in nylon-6,6. Adding carbon black and synthetic graphite particles caused the impact strength of the composite to be lower than that of the neat polymer (original: 45.3; replicate: 43.3 J/m). However, when 20 wt % (13.7 vol %) or more of carbon fiber was added, the impact strength increased, which is most likely due to the increased crack propagation length needed to cause composite failure. This increase in impact strength with carbon fiber content has been reported elsewhere.[31]

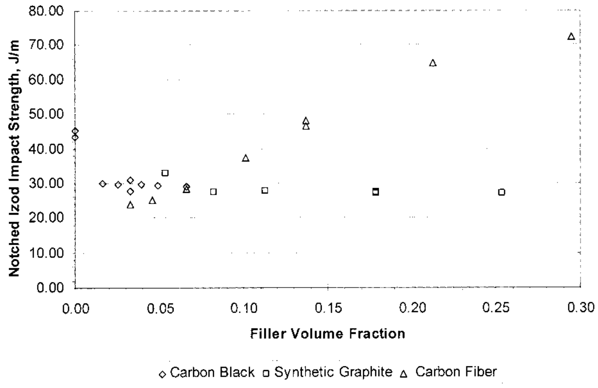

Figure 7 Notched Izod impact strength of single filler composites.

Factorial design analysis

Tables VI–VIII show the tensile modulus, ultimate stress, and strain at ultimate stress for the factorial design formulations in nylon-6,6. Table IX shows the Izod impact strength for the factorial design formulations in nylon-6,6. Using the results shown in Tables VI–IX, an analysis of the factorial design was completed. This was performed using the Minitab™ release 13 Statistical Software package. For this analysis, the effects, as well as *T* (often designated *t*) and *P* (also often designated as *p*) values for the results were calculated. High *T* values (refers to the student-t distribution) and low *P* values (smallest level of significance that would lead to the rejection of the null hypothesis) indicate that the factor being studied (e.g. carbon fibers) has a significant effect on the property (e.g. tensile modulus) being investigated.[37] For all statistical calculations, the 95% confidence level was used.

Factorial designs were used in the project since they are the most efficient type of experiment to determine the effect of each filler and any possible interactions among fillers. By using factorials, one can determine the effect that each factor (filler) has on the system by calculating a single value to quantify the change in tensile/impact properties as the weight percent of filler is increased. These calculated effects can then be ranked to determine which fillers and combinations of fillers produced the largest change.

TABLE VI
Tensile Modulus Results for Factorial Design Formulations

Formulation	Tensile modulus (GPa) Original	Tensile modulus (GPa) Replicate
No filler	3.28 ± 0.10 $n = 5$	3.30 ± 0.15 $n = 5$
CB	3.65 ± 0.09 $n = 6$	3.71 ± 0.08 $n = 5$
SG	5.91 ± 0.19 $n = 6$	6.45 ± 0.04 $n = 5$
CF	14.54 ± 1.57 $n = 5$	13.37 ± 0.83 $n = 5$
CB*SG	8.10 ± 0.70 $n = 7$	8.16 ± 0.36 $n = 6$
CB*CF	13.51 ± 1.10 $n = 7$	13.66 ± 1.73 $n = 8$
SG*CF	18.09 ± 2.16 $n = 5$	19.44 ± 1.77 $n = 7$
CB*SG*CF	21.09 ± 1.34 $n = 7$	20.17 ± 1.52 $n = 6$

TABLE VII
Ultimate Tensile Stress Results for Factorial Design Formulations

Formulation	Ultimate tensile stress (MPa) Original	Ultimate tensile stress (MPa) Replicate
No filler	86.67 ± 0.30 $n = 5$	85.23 ± 0.55 $n = 5$
CB	65.55 ± 2.37 $n = 6$	64.67 ± 4.35 $n = 5$
SG	61.15 ± 0.79 $n = 6$	62.86 ± 0.60 $n = 5$
CF	197.29 ± 2.61 $n = 5$	195.01 ± 0.59 $n = 5$
CB*SG	62.97 ± 1.33 $n = 7$	63.13 ± 0.76 $n = 6$
CB*CF	177.88 ± 4.66 $n = 7$	162.40 ± 5.43 $n = 8$
SG*CF	110.07 ± 2.51 $n = 5$	110.70 ± 5.75 $n = 7$
CB*SG*CF	85.57 ± 6.63 $n = 7$	88.56 ± 2.16 $n = 6$

Tensile results

The effects and the *T* and *P* values for tensile modulus of the composites are given in Table X, which shows the values for all filler combinations. Further examination of Table X yields some important information regarding the effects that single fillers and combinations of fillers have on the tensile modulus. First, all of the statistically significant ($P < 0.05$) effect terms are positive, which indicates that the addition of any filler increases the composite tensile modulus. Second, carbon fiber, followed by synthetic graphite and the combination of synthetic graphite and carbon fiber, causes the largest increase (largest effect term) in composite tensile modulus. The effects of carbon black and the combination of carbon black and synthetic graphite particles follow, and are essentially the same (Table X). All of the results mentioned in this paragraph are statistically significant at the 95% confidence level ($P < 0.05$). The results for resins containing the combination of carbon black and carbon fiber and those containing all three fillers were not statistically significant ($P > 0.05$). The statistically significant results for the

TABLE VIII
Strain at Ultimate Tensile Stress for Factorial Design

Formulation	Strain at ultimate tensile stress (%) Original	Strain at ultimate tensile stress (%) Replicate
No filler	4.06 ± 0.28 $n = 5$	3.82 ± 0.11 $n = 5$
CB	1.91 ± 0.09 $n = 6$	1.84 ± 0.19 $n = 5$
SG	1.71 ± 0.14 $n = 6$	1.78 ± 0.11 $n = 5$
CF	2.41 ± 0.14 $n = 5$	2.45 ± 0.08 $n = 5$
CB*SG	1.20 ± 0.06 $n = 7$	1.13 ± 0.07 $n = 6$
CB*CF	1.90 ± 0.04 $n = 7$	1.95 ± 0.30 $n = 8$
SG*CF	1.05 ± 0.17 $n = 5$	1.02 ± 0.20 $n = 7$
CB*SG*CF	0.55 ± 0.10 $n = 7$	0.57 ± 0.06 $n = 6$

TABLE IX
Notched Izod Impact Strength Results for Factorial Design Formulations

Formulation	Impact strength (J/m)	
	Original	Replicate
No filler	45.3 ± 3.6 $n = 16$	43.3 ± 3.4 $n = 15$
CB	27.8 ± 2.5 $n = 15$	30.8 ± 1.7 $n = 15$
SG	27.4 ± 1.1 $n = 14$	27.1 ± 1.0 $n = 15$
CF	46.4 ± 2.4 $n = 15$	48.1 ± 1.7 $n = 15$
CB*SG	19.9 ± 2.8 $n = 15$	20.1 ± 2.4 $n = 14$
CB*CF	39.7 ± 1.8 $n = 15$	36.8 ± 1.8 $n = 15$
SG*CF	39.7 ± 0.8 $n = 15$	40.1 ± 1.2 $n = 15$
CB*SG*CF	29.3 ± 0.6 $n = 15$	27.3 ± 2.1 $n = 15$

synthetic graphite/carbon fiber composites and the carbon black/synthetic graphite composites show that there is an effect on tensile modulus when different fillers are combined. This means that, for example, when synthetic graphite and carbon fiber were combined and added to nylon, the tensile modulus of the composite increased more than what would be expected from the individual additive effect of synthetic graphite and carbon fiber.[37] These results show that interactions do have an effect on the tensile modulus of the composites. It is possible that additional pathways are present between the different fillers to transfer the load among the highly branched, high surface area carbon black, the synthetic graphite particles, and the carbon fiber that results in higher composite tensile modulus.

Table XI shows the effects and the T and P values for ultimate tensile stress for the nylon-6,6 based composites, showing the values for all of the filler combinations. Further examination of Table XI yields some important information regarding the effects that single fillers and combinations of fillers have on the ultimate tensile stress. Of all the single fillers, only carbon fibers caused an increase in ultimate tensile stress (positive effect term). Carbon black and synthetic graphite caused the composite ultimate tensile stress to decrease. Based on the effect terms, synthetic graphite caused the largest decrease in composite ultimate tensile stress, followed by the combination of synthetic graphite particles and carbon fibers, then carbon black, and then the combination of carbon black and carbon fiber. The next largest effect term, that for the carbon black/synthetic graphite combination, was positive, which indicates a higher composite ultimate tensile stress. The lowest effect term was calculated for the resin with all three fillers. All results for the single and combined fillers are statistically significant at the 95% confidence level ($P < 0.05$). The statistically significant results for the two and three way interactions indicate that the combination of different fillers affects the ultimate tensile stress. This means that, for example, when synthetic graphite and carbon fibers were combined and added to nylon-6,6, the ultimate tensile stress of the composite decreased (negative effect term) more than what would be expected from the individual additive effect of synthetic graphite and carbon fiber.

The effects and T and P values for strain at ultimate tensile stress for the composites are given in Table XII, which shows the values for all filler combinations. Further examination of Table XII yields some important information regarding the effects that single fillers and combinations of fillers have on tensile strain. For all single fillers, all of the effect terms are negative, which indicates that the addition of any filler decreases the composite tensile strain. Synthetic graphite particles caused the largest decrease in composite tensile strain, followed by carbon black, and then carbon fibers. The results for all single fillers, as well as the

TABLE X
Factorial Design Analysis for Tensile Modulus

Term	Effect	T	P
Constant		84.31	0.000
CB	0.96	3.66	0.006
SG	4.79	18.33	0.000
CF	11.41	43.64	0.000
CB*SG	0.95	3.62	0.007
CB*CF	−0.21	0.81	0.443
SG*CF	1.13	4.32	0.003
CB*SG*CF	0.17	0.64	0.539

TABLE XI
Factorial Design Analysis for Ultimate Tensile Stress

Term	Effect	T	P
Constant		104.13	0.000
CB	−17.28	8.57	0.000
SG	−48.71	24.16	0.000
CF	71.91	35.66	0.000
CB*SG	6.14	3.05	0.016
CB*CF	−7.38	3.66	0.006
SG*CF	−35.71	17.71	0.000
CB*SG*CF	−4.80	2.38	0.045

TABLE XII
Factorial Design Analysis for Strain at Ultimate Tensile Stress

Term	Effect	T	P
Constant		105.29	0.000
CB	−0.91	26.01	0.000
SG	−1.42	40.65	0.000
CF	−0.69	19.91	0.000
CB*SG	0.38	10.87	0.000
CB*CF	0.42	11.95	0.000
SG*CF	0.04	1.04	0.329
CB*SG*CF	−0.36	10.44	0.000

TABLE XIII
Factorial Design Analysis for Notched Izod Impact Strength

Term	Effect	*T*	*P*
Constant		102.69	0.000
CB	−10.71	16.03	0.000
SG	−10.91	16.33	0.000
CF	8.21	12.29	0.000
CB*SG	1.29	1.93	0.090
CB*CF	0.41	0.62	0.554
SG*CF	2.26	3.39	0.010
CB*SG*CF	−2.59	3.87	0.005

carbon black/carbon fiber, carbon black/synthetic graphite combinations and the combination of all three fillers, were statistically significant at the 95% confidence level ($P < 0.05$). Only the synthetic graphite/carbon fiber resin result was not statistically significant ($P > 0.05$). The statistically significant results for two of the two way and the three way interaction indicate that there is an effect on strain at ultimate tensile stress when different fillers are combined.

Notched Izod impact strength results

The effects and the *T* and *P* values for Izod impact strength of the composites are given in Table XIII, which shows the values for all filler combinations. Of all single fillers, the results for all of which were statistically significant, only the addition of carbon fiber caused the impact strength to increase (positive effect term). Synthetic graphite particles and carbon black caused a large decrease (negative effect term) in impact strength. The values for the synthetic graphite/carbon fiber combination, as well as those for the combination of all three fillers, were also statistically significant. The three filler interaction had a negative effect term, indicating that, when the three different fillers are combined in a resin, the notched Izod impact strength decreases more than would be expected from the individual additive effect of each filler.

A prior project investigated the effects of fillers on the tensile and impact properties of a composite containing the same nylon, carbon black and synthetic graphite particles but a different carbon fiber. In the past project, BP/Amoco milled (200 μm long) pitch based carbon fiber, ThermalGraph DKD X, was used.[30] Comparing the results from this present study to the one previously conducted yields some interesting observations. When looking at the composites filled only with carbon fibers, the resins containing 20 wt % (11.7 vol %) ThermalGraph DKD X had an ultimate tensile strength and impact strength of 97.7 MPa and 28 J/m, respectively, as compared to 196 MPa and 47 J/m for those containing 20 wt % (13.7 vol %) Fortafil 243. Also, the composites containing 40 wt % (26.1 vol %) ThermalGraph DKD X had an ultimate tensile strength of 120.5 MPa and an impact strength of 31.7 J/m as compared to 229 MPa and 72.4 J/m for those containing 40 wt % (29.5 vol %) Fortafil 243. The tensile modulus of the composites containing 20 wt % ThermalGraph DKD X (12.0 GPa) and 20 wt % Fortafil 243 (14.0 GPa) were similar, as were those for 40 wt % ThermalGraph DKD X (24.1 GPa) and 40 wt % Fortafil 243 (23.3 GPa).

When considering the factorial design formulations, the resin containing carbon black and ThermalGraph DKD X had an ultimate tensile stress of 87.1 MPa and an impact strength of 25.0 J/m. The resin containing carbon black and Fortafil 243 had an ultimate tensile stress of 177.9 MPa and an impact strength of 39.7 J/m.

The composite containing synthetic graphite particles and ThermalGraph DKD X had an ultimate tensile stress of 80.9 MPa and an impact strength of 27.1 J/m. The resin containing synthetic graphite particles and Fortafil 243 had an ultimate tensile stress of 110.1 MPa and an impact strength of 39.7 J/m. In both cases, it is apparent that the resin containing the surface treated Fortafil 243 had a higher ultimate tensile stress and impact strength.

The length of the carbon fibers in the composite can have an important effect on composite tensile strength. The carbon fiber length in the composites containing the surface treated Fortafil 243 was typically 110 μm, as compared to approximately 100 μm for those containing the milled pitch based fiber ThermalGraph DKD X. Hence, the lengths of these fibers are similar.

Nanoscratch tests were also performed on samples containing 20 wt % Fortafil 243 in nylon-6,6 and 20 wt % ThermalGraph DKD X in nylon-6,6, and the results were compared. Scratch tests performed on a heterogenous material under constant normal load gives the localized compliance of the material, so it is possible to detect the filler rich and matrix rich areas along the scratch path. A shallow scratch depth indicates a high stiffness (filler rich) material. A higher scratch depth indicates a lower stiffness (matrix rich) material. Since the size of the scratch tip is large compared to the diameter (7.3 μm) of the carbon fibers, it is not possible to record the load-displacement response as the tip travels from the matrix onto a single fiber. Figure 8 shows the tip displacement as a function of scratch distance for the composite sample containing 20 wt % Fortafil 243 in nylon-6,6. Typically, the displacement values corresponding to a depth of at least 3000 nm indicate a matrix rich region. The displacement values corresponding to a fiber rich region are typically less than 2000 nm. A transition region exists between the fibers and the matrix.

A similar observation can be made from a plot of friction force versus scratch distance.[38] Higher friction

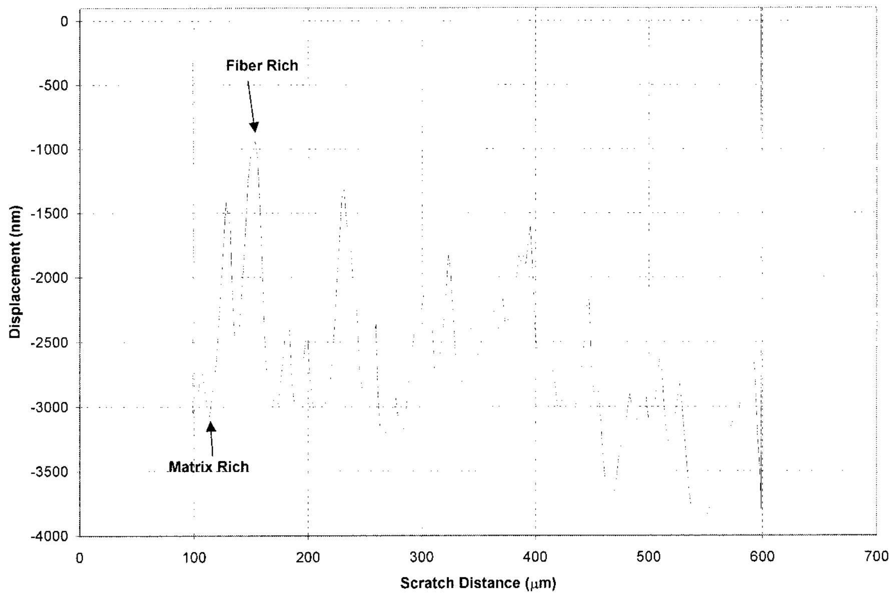

Figure 8 Displacement normal to specimen surface under 40 mN normal force for composite containing 20 wt % Fortafil 243 carbon fibers in nylon-6,6.

forces are measured in fiber rich areas versus matrix rich areas. To highlight the difference in the response of two material systems to a scratch test, the friction force is normalized with respect to the maximum force recorded during its respective test. For the composite containing 20 wt % ThermalGraph DKD X in nylon-6,6 (Fig. 9) the maximum force recorded was 12.0 mN. For the composites containing 20 wt % Fortafil 243 in nylon-6,6 (Fig. 10), the maximum force was 10.9 mN. A comparison of the normalized friction force along the scratch length (or distance) for the composites containing 20 wt % ThermalGraph DKD X (Fig. 9) or 20 wt % Fortafil 243 (Fig. 10) reveals that the difference in the friction force between the matrix and fiber rich areas is much larger for the composite containing Fortafil 243. Figure 9 shows that the maximum change in the normalized friction force is about is about 10% of the maximum for the ThermalGraph DKD X/nylon composite. Figure 10 shows that this change is much higher for the Fortafil 243/nylon composite. The

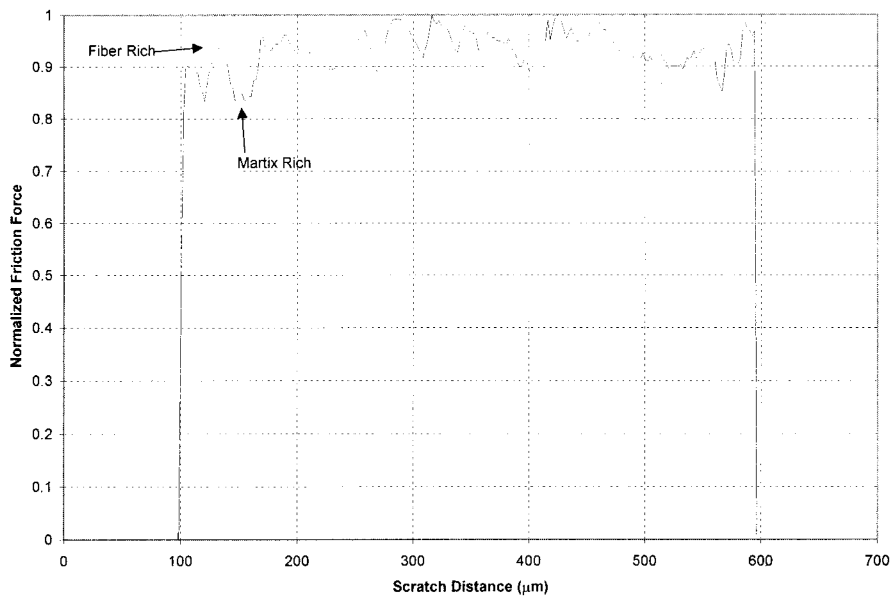

Figure 9 Normalized friction force along scratch distance for composite containing 20 wt % ThermalGraph DKD X carbon fibers in nylon-6,6.

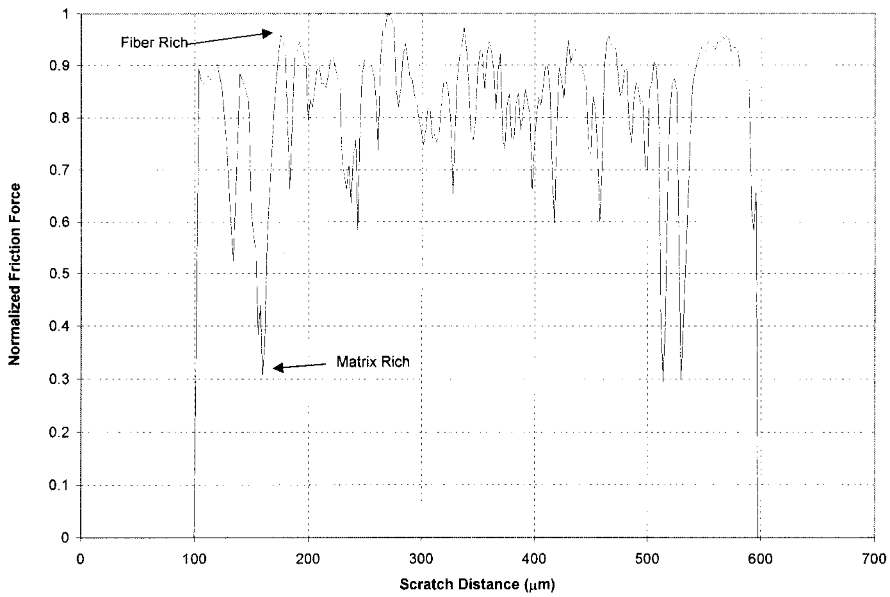

Figure 10 Normalized friction force along scratch distance for composite containing 20 wt % Fortafil 243 carbon fiber in nylon-6,6.

change in the friction force along the scratch can be interpreted as a measure of the resistance to the motion of the scratch tip through the material. As fiber rich areas are approached, this force increases, indicating higher strength (fiber rich) in the material in that vicinity. By comparing the scratch test results, one can conclude that the adhesion in the Fortafil 243/nylon system, with a higher change in the friction force, is better than the adhesion in the ThermalGraph DKD X/nylon system. This is consistent with the higher ultimate tensile strength and impact strength results for the composites containing Fortafil 243 carbon fibers. Although more analysis is needed to verify the correlation of the scratch test results to adhesion, these tests seem to be a potential measure for comparison of adhesion among different fiber–matrix systems.

More information concerning the fiber–matrix adhesion can be determined by considering the surface polarity and heteroatoms present on the fiber surface. The surface polarity and amount of oxygen present on the fiber surface was higher for the Fortafil 243 (surface polarity: 30.1%, 8.5 atomic % oxygen) versus ThermalGraph DKD X (surface polarity: 24.6%, 3.7 atomic % oxygen) (26). Figure 11 shows the ESEM photomicrograph at a magnification of 1000× of the tensile fracture surface of the composites containing 20 wt % ThermalGraph DKD X in nylon-6,6. Figure 12 illustrates the ESEM photomicrograph at a magnification of 1000× of the tensile fracture surface of the composites containing 20 wt % Fortafil 243 in nylon-6,6. Figure 12 appears to show that nylon matrix material adhering to the Fortafil 243 carbon fiber surface, indicating good fiber–matrix adhesion. In contrast, in Figure 11 the matrix material does not appear to be adhering to the ThermalGraph DKD X carbon fiber surface, which could indicate poor fiber–matrix adhesion. Often, carbon fibers are surface treated to improve fiber–matrix adhesion, which increases the composite tensile strength.[39] The composite tensile modulus is often unaffected by improved adhesion.[39] It has also been shown that improved filler–matrix adhesion can improve the fracture toughness of short fiber composites.[39–42] Based on the results from these two projects, as well as the ESEM photomicrographs and nanoscratch results, it is likely that the increased heteroatoms present on the surface of the Fortafil 243 result in improved adhesion to the nylon matrix ma-

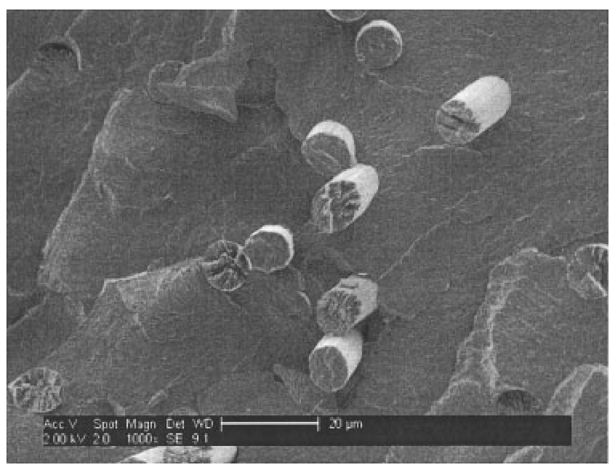

Figure 11 ESEM photomicrograph at 1000× magnification of tensile fracture surface of composite containing 20 wt % ThermalGraph DKD X in nylon-6,6.

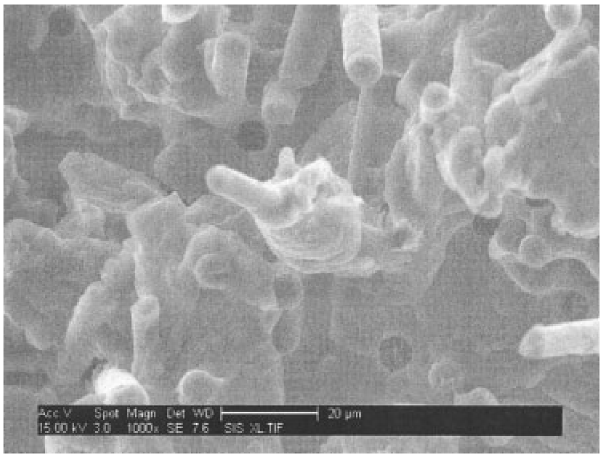

Figure 12 ESEM photomicrograph at 1000× magnification of tensile fracture surface of composite containing 20 wt % Fortafil 243 in nylon-6,6.

terial, which increases composite ultimate tensile stress and impact strength.

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 115 μm and 16, respectively. However, the length (typically 60 to 70 μm) and aspect ratio (typically 1.7 to 1.8) of the synthetic graphite in the composite specimens remain similar to those of the as-received material. This high purity, synthetic graphite likely maintained its size better than the carbon fibers since the as-received synthetic graphite material had a smaller length and aspect ratio. Concerning orientation, due to the polymer flow into the mold during the injection molding process, the synthetic graphite particles and carbon fibers were mainly oriented in the longitudinal tensile direction.

Adding increasing amounts of filler increases the composite thermal and electrical conductivity and the tensile modulus. However, trade-offs with other mechanical properties exist. For example, carbon fiber was the only filler that caused the composite ultimate tensile stress and impact strength to increase. Adding any filler caused the composite strain at ultimate stress to decrease.

The use of factorial design to analyze the tensile and impact results allows ranking of the effects of single fillers and combinations of different fillers. In many cases, combining two and three different fillers caused a statistically significant effect. For example, concerning the tensile modulus of nylon-6,6, the most significant combination was that of synthetic graphite/carbon fibers, followed by carbon black/synthetic graphite. This means that, for example, when synthetic graphite and carbon fibers were combined and added to nylon, the tensile modulus of the composite increased more than would be expected from the individual additive effects. It is possible that additional pathways are present between the different fillers to transfer the load among the highly branched, high surface area carbon black, the synthetic graphite particles and carbon fibers, resulting in higher composite tensile modulus.

The ESEM photomicrographs and nanoscratch results presented here suggest that better fiber–matrix adhesion is present if the carbon fibers are surface treated. Also, from comparing the tensile and impact results from a prior project[30] to the current results, it appears that an increased number of heteroatoms present on the carbon fiber surface likely improve composite ultimate tensile stress and impact strength.

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