

Enhancing the Strength of Polypropylene Fibers with Carbon Nanotubes

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ABSTRACT: Single-walled carbon nanotubes were added to two different grades of polypropylene to produce composites. The composites were then melt-spun into fibers, and the fibers were tested with both a conventional tensile pull tester and dynamic mechanical analysis. The changes in tensile properties were related to the grade of polypropylene used. In addition to fibers being made from the mixes, coarse extrudates (i.e., undrawn, gravity-spun filaments) were also produced. Density measurements on these extrudates

showed that the addition of nanotubes increased the composite density in a highly nonlinear manner, which suggested interaction between the polypropylene and the carbon nanotubes. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2926–2933, 2004

Key words: polypropylene (PP); fibers; nanocomposites; mechanical properties; high performance polymers

INTRODUCTION

The incorporation of carbon nanotubes (CNTs) into polymer matrices is presently an active field of research.^{1–6} The impressive physical, thermal, and electrical properties of CNTs are believed to have the potential to dramatically improve the properties of polymers. The commercialization of CNT/polymer composites has already occurred;⁷ nanotubes are added to polymers to improve their electrical properties rather than their mechanical or thermal properties. Many researchers have tried to improve the mechanical properties of various polymers through CNTs; however, the true potential of the nanotubes has not yet been realized.⁸ Numerous researchers have shown large improvements in the moduli of CNT composites, but few researchers have shown any improvement in their ultimate strength.

Melt-spinning is the most common method for producing man-made fibers. Melt-spinning is quite rapid; spinning speeds of 6000 m/min and greater are common.⁹ A similar process known as melt-blowing can involve speeds of 30,000 m/min. Because of the economies involved with these high speeds, billions of dollars worth of melt-spun fibers are produced every year.

Fiber strength is often a dominant factor in the use of fibers. Presently, melt-spun fibers have maximum tensile strengths of about 9 g/denier. This strength is quite sufficient for tire cord, ropes, and many other uses. If there is a need for higher strengths, solutions-spun aramid fibers and gel-spun polyethylene fibers have

strengths of about 22 g/denier. Unfortunately, these fibers are very expensive, and this expense is mainly due to the fact that solution or gel-spinning are much more expensive than conventional melt-spinning because the former is slower and involves a solvent.

The goal of our research program is to add CNTs to polypropylene (PP) to produce a composite material that can be spun into fibers via straightforward melt-spinning. If a large increase in strength can be achieved with CNTs, the composite PP fibers could potentially be used as a competitor for aramid and other types of superstrong fibers that are produced through much more complicated, and expensive, production techniques.

Fibers are of particular interest in our research because the stresses applied during spinning can align the nanotubes along the fiber axis.¹⁰ Because of the high tensile strength and modulus of nanotubes, a high degree of nanotube alignment in the axial direction can potentially produce a very strong polymer fiber.

In this study, composites of PP fibers with nanotubes were produced with varying levels of CNTs. A solution process that was developed previously⁸ was used to disperse the nanotubes in the polymer matrix. Of interest were both the increase in the fiber break strength (tenacity) and the stiffness (modulus) of the fibers.

EXPERIMENTAL

Material preparation

Carbolex AP-grade (as prepared grade) single-walled CNTs were used in the experiments. Carbolex AP-

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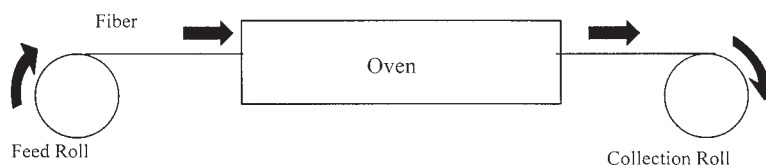


Figure 1 Schematic of the postdrawing process.

grade nanotubes that contain about 50–70% single-walled CNTs and are produced by a carbon arc process; the material contains both carbon and metallic impurities. The CNTs were used as received, with no additional purification.

Two grades of isotactic PP, Fina 3960 and Fina 3860X, were used in this work. Fina 3960 is a very-low-viscosity (melt-flow rate = 350–360) resin intended for nonwoven fiber production. Fina 3860X is a higher viscosity (melt-flow rate = 100) grade also meant for fiber production. Throughout this article, Fina 3960 is referred to as a high-melt-flow-rate (HMFR) resin, and Fina 3860X is referred to as a low-melt-flow-rate (LMFR) resin.

CNT-PP composites were manufactured by an ultrasonic solution process. For each concentration of CNTs, 75 mL of room-temperature decalin was poured into a 250-mL beaker. Next, the appropriate mass of CNTs was added. A Fisher Scientific (Pittsburgh, PA) model 550 sonic dismembrator was then used to disperse the CNTs into the decalin. The sonic mixer was operated for 1 h at power setting 4. Although no external heat was applied, the mixing heated up the beaker's contents to approximately 45°C over the course of the first hour of sonication. After the first mixing was complete, 20 g of PP pellets (either HMFR or LMFR) and an additional 25 mL of decalin were added to the mixture. The sonic mixer was then started for another hour, and a hotplate was used to heat the beaker and help dissolve the PP. The final temperature of the mixture reached approximately 140°C. When the mixing was complete, the beaker was removed from the hotplate and allowed to cool to room temperature. The resulting product was a soft, solid mass that ranged from gray to black in color (depending on the nanotube concentration). This solid was allowed to dry at room temperature for 24 h before the solid was subjected to vacuum drying.

The sample was placed in a vacuum oven set at 100°C and with a vacuum of about 17 kPa (~2.5 psi); under these conditions, the decalin was removed without the melting of the polymer sample. The samples were dried to a constant weight in a period of about 4 to 7 days. The residual decalin content was well below 1%. During drying, the samples were occasionally mixed and broken up with a spatula to speed drying. The fully dried polymer consisted of solid chunks that were easily broken up; this friability aided the charging of the composite into the spinning device.

Spinning

The spinning of the nanotube composites was done with a ram extruder. The molten polymer was forced through a spinneret with a constant speed drive. The spinneret had a capillary with a 1.27 mm diameter and a 50 mm length. Fiber take-up was accomplished with an electrically driven take-up roll with a 15-cm (6-in.) diameter. Spinning was conducted by the preheating of the barrel and capillary to 190°C. The polymer sample was then charged into the extruder barrel. After charging, the samples were allowed to sit for a few minutes to both allow the polymer to melt and permit the air bubbles to surface. Then, the ram was started, and the polymer was extruded through the capillary. The fiber samples were collected upon the spinning take-up roll. When these samples were not subjected to any further processing, the samples were called as-spun fibers. The typical diameter of our as-spun fibers was about 50–60 μm . In a secondary spinning experiment, the polymer was simply pushed through the capillary with no wind-up roll below the capillary. This procedure was used to produce thick (diameter = 0.5–1.5 mm) extrudate for density measurements. Extrudates were collected on an aluminum plate that was held a few centimeters below the capillary discharge. Because these extrudates were not subjected to the stresses of spinning, the extrudates showed the effect of CNTs in lightly stressed PP.

Postdrawing

Postdrawing is the process of stretching, in a controlled manner, fibers in a separate step after initial fiber production. In polymer fibers, postdrawing can lead to increased orientation and crystallization and an improvement in both strength and modulus. Postdrawing in this study was accomplished with two 6.5-cm diameter rolls with independent speed controls. Between the rolls was a small oven that the fiber passed through as it was drawn. A schematic of the process used is shown in Figure 1. The oven was 37 cm (14.6 in.) long, constructed of stainless steel, and heated with electric cartridge heaters placed in the top and bottom of the oven. The fiber was fed through a slot in one end of the oven and pulled out through a similar slot on the other end. The temperature was controlled with thermocouples placed in the oven air. There was some variation in oven temperature, but all

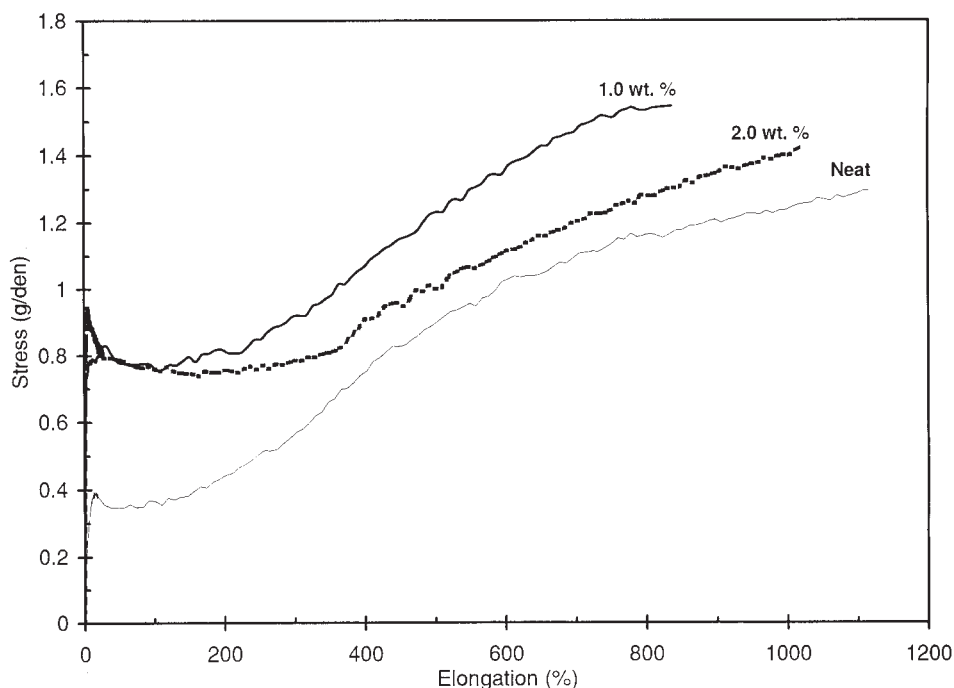


Figure 2 Representative stress–strain curves for postdrawn LMFR PP fibers with different CNT concentrations.

of the samples were drawn at temperatures between 105 and 115°C. We loaded the fiber into the drawing device by threading the fiber from the feed roll to the draw roll with the top of the oven open. After loading, the oven top was closed, and the oven was allowed to come to a steady temperature before the rolls were started. At the start of the drawing process, the feed roll was set to 1 m/min (surface speed) and the draw roll was set to a higher value (usually about 3 m/min). Once started at these slower speeds, the draw-roll speed was then increased until the fiber was almost broken. The postdraw ratio was the ratio of the draw-roll speed to the feed-roll speed. This ratio was also equal to the square of the initial (as-spun) fiber diameter divided by the square of the final (drawn) fiber diameter. Postdraw ratios of up to 9:1 were achieved in this study, and the resulting final fiber diameters were in the range 20–30 μm . In all cases, the addition of CNTs reduced the maximum achievable postdraw ratio. No fiber with CNTs could be postdrawn with a ratio greater than 7:1.

Fiber diameter measurement

The fibers diameters were measured with a Nikon LaboPhot2-Pol polarizing microscope equipped with an objective micrometer. Calibration was accomplished with a graduated micrometer slide. To measure the diameter of a fiber, a short length of fiber was placed onto a slide. The slide was then covered with a cover glass and loaded onto the microscope stage. At

an overall magnification at 400 \times , the objective micrometer was able to measure the diameter of the fiber with 0.25- μ resolution. The examination of the fibers under light microscopy also provided us with a chance to qualitatively inspect the dispersion of nanotubes within the fibers. Generally, if the dispersion was poor, the final properties were also poor. However, good dispersion did not ensure good properties.

Polymer density measurement

The densities of both the extrudate and the as-spun fiber were measured with a Techné (Princeton, NJ) DC-4 glass density gradient column. After the column was filled with a gradient of ethanol and deionized water, four calibrated glass floats were carefully added to the column; these floats were used to scale the gradient over the range of interest. The column was kept at ambient temperature ($\sim 22^\circ\text{C}$) throughout the measurements. Up to three samples at once were placed in the column; samples were identified via length and diameter. At least three replicate samples were tested for each set of operating conditions, and at least three readings were done for each individual sample. To calculate the densities, the positions of the glass floats were plotted on the abscissa of a graph, whereas the known float densities were plotted on the ordinate. A least-squares line was fitted through the points. The densities of the fiber samples were then determined from this line on the graph.

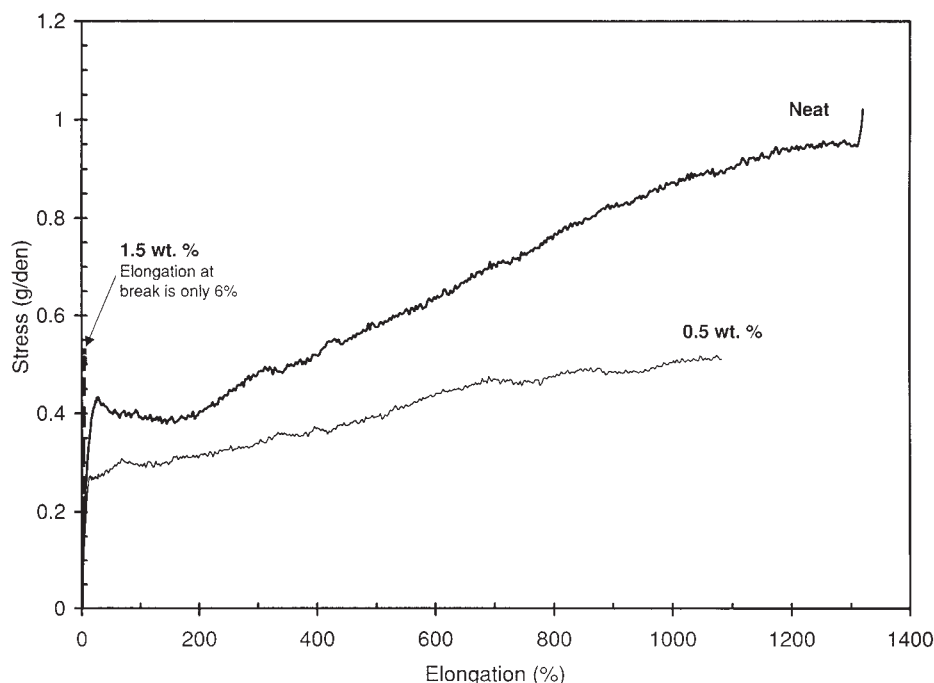


Figure 3 Representative stress–strain curves for as-spun LMFR PP fibers with different CNT concentrations.

Tensile strength measurements

Stress–strain curves for all of the samples were measured with an Instron (Canton, MA) model TT-B-L testing machine equipped with a type BT load cell. The gauge length used was 2.29 cm (0.902 in.), and the crosshead speed was 2.54 cm/min (1 in./min). The fibers were held by an Instron model 2714 pneumatic grips. Data were recorded with a PC equipped with custom data-acquisition software. The outputs from the tester were the load on the fiber in grams and the time elapsed since the start. These data were converted to graphs of tenacity (g/denier) versus elongation (%). Tenacity was related to the stress on the fiber and the fiber density via the following equation:

$$T = 7.82 \times 10^{-5} \frac{\sigma}{\rho} \tag{1}$$

where σ is the stress on the fiber (psi), ρ is the density of fiber (g/cm³), and T is the tenacity (g/denier).

Dynamic mechanical analysis (DMA)

The fiber samples were also tested via DMA. DMA permitted the measurement of the linear viscoelastic properties across a wide temperature range. The tests were conducted with a Rheometric Scientific (Piscataway, NJ) model RSA II. Each sample was loaded with monofilament grips, and the sample was subjected to a preload of 1 g. The storage modulus (E') and loss modulus (E'') were measured at a fixed frequency of 10

rad/s (1.59 Hz) over a temperature range of -100°C to the melting of the fiber near 160°C . To more closely examine the effect of CNTs in the glass-transition region, the scans were run at a higher temperature resolution in the range -25 to 10°C .

RESULTS AND DISCUSSION

Tensile strength measurements: as-spun fibers

The as-spun fibers from both grades of PP showed typical behavior for neat material. Stress–strain curves showed that the fibers had a high initial modulus then a sharp yield and then exhibited stretching to very large elongations at break. The addition of CNTs to the fibers did not change this behavior qualitatively;

TABLE I
Comparison of As-Spun CNT/PP Fibers

Nanotube composition (wt %)	Tenacity (g/denier)	Elongation at break (%)
LMFR PP		
0 (neat)	1.19	615
0.5	1.11	710
1.0	1.55	818
2.0	1.48	870
HMFR PP		
0 (neat)	1.02	1320
0.5	0.51	1081
1.0	0.27	11
1.5	0.57	6
2.0		Not spinable

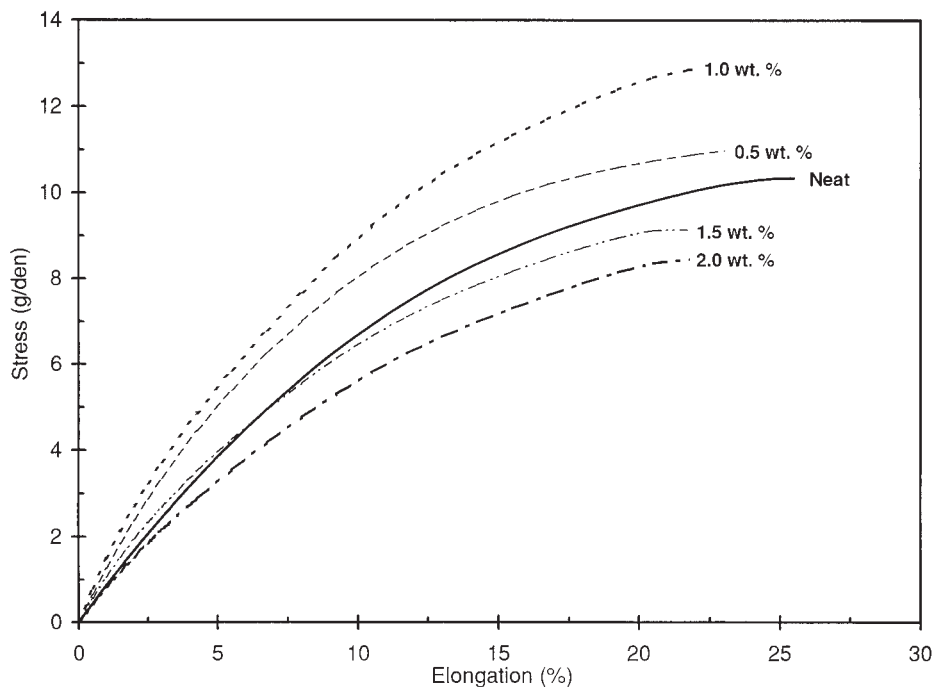


Figure 4 Representative stress–strain curves for postdrawn LMFR PP fibers with different CNT concentrations.

however, the elongations at break were lower in the composite samples. Figures 2 and 3 show representative stress–strain curves for both LMFR and HMFR as-spun samples. From the figures, two important points become clear. First, the addition of CNTs had different effects on the two different grade of PP. In

the LMFR samples, the addition of CNTs led to an increase in the tensile strength of the fiber. In the HMFR PP samples, the addition of nanotubes had the opposite effect. Another remarkable result was that the addition of 1.5% nanotubes to the HMFR resin led to an as-spun fiber with an elongation at break of only

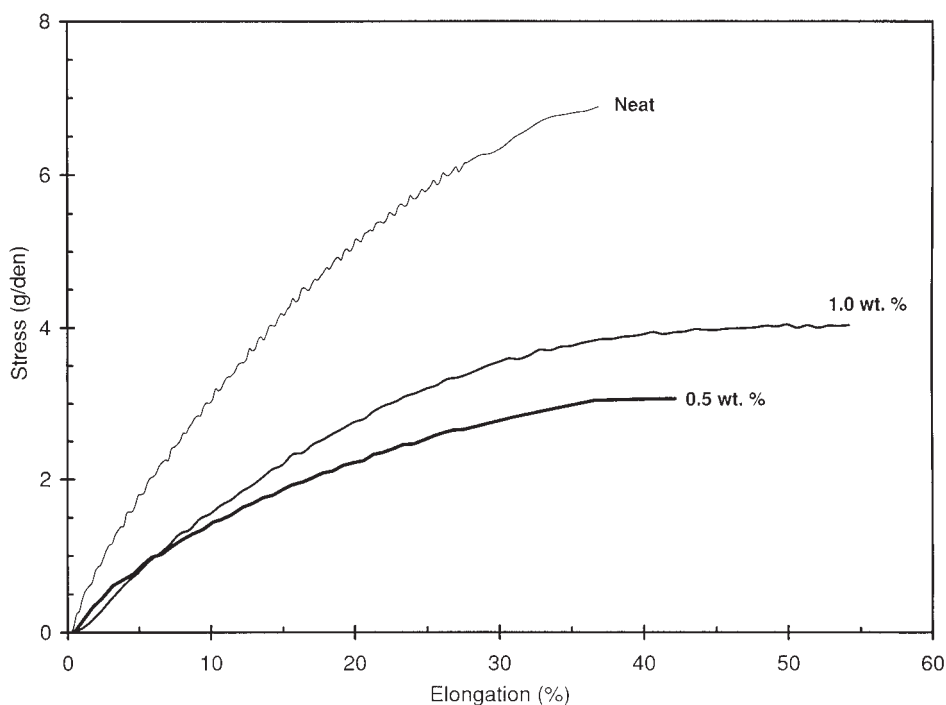


Figure 5 Representative stress–strain curves for postdrawn HMFR PP fibers with different CNT concentrations.

TABLE II
Comparison of Postdrawn CNT/PP Fibers

Nanotube composition (wt %)	Tenacity (g/denier)	Elongation at break (%)
LMFR PP		
0 (neat)	9.0	27.1
0.5	10.6	19.1
1.0	13.0	26.7
1.5	9.36	23.3
2.0	7.85	23.0
HMFR PP		
0 (neat)	6.88	36.8
0.5	3.06	42.1
1.0	4.03	54
1.5		Not drawable
2.0		Not spinable

6%, in stark contrast to the neat material that stretches as high as 1300% before breaking. This behavior was apparent during fiber spinning: the fibers were brittle and snapped frequently during spinning. Table I gives comparisons of both tenacity and elongation at break for the as-spun fibers.

Tensile strength measurements: postdrawn fibers

For postdrawn fibers from LMFR PP, additions of 0.5 and 1.0% CNTs increased the strength of the fibers. Figure 4 shows the stress–strain curves for postdrawn fibers for 0% (neat), 0.5%, and 1.0% CNTs. The addition of CNTs significantly increased the strength and slightly reduced the elongation at break. Individual fibers containing 1% CNTs showed strengths of up to 14.5 g/denier with an average strength of approximately 13 g/denier. This was a nearly 45% increase in the ultimate strength of the fiber at this low addition level. The addition of CNTs in concentrations of 1.5 and 2.0% resulted in decreases in strength and elon-

gation compared to the neat fiber (see Fig. 4). The fibers with higher CNT concentrations were more brittle and more difficult to postdraw. Although a neat or low-concentration fiber could be drawn with postdraw ratios of up to 9:1, higher concentration fibers often had maximum postdraw ratios of 6:1 or lower.

Postdrawn HMFR PP fibers showed significantly different behavior than the LMFR fibers. For the HMFR fibers, the addition of CNT decreased the ultimate strength of all of the fibers produced. However, the average strength of the 1.0% fibers was higher than that of the 0.5% fibers, as shown in Figure 5. It was not possible to test fibers with higher concentrations because, with higher concentrations, the as-spun fibers were far too brittle to be postdrawn successfully. Table II shows the average elongation at break and tenacity of both HMFR and LMFR postdrawn fibers.

DMA

DMA results followed the same trends as those discussed previously for conventional tensile testing. Table III shows the averaged results for neat and 1.0% nanotube fibers, both as-spun and postdrawn.

E' could be increased through the addition of CNTs. However, there were temperature limits to this increase. At higher temperatures, E' of the postdrawn fibers actually decreased with the addition of CNTs. As-spun fibers showed the greatest increases in E' with the addition of 1% CNTs. Consistent with the tensile tests, postdrawing yielded a far stiffer fiber, with or without CNTs. Also, when compared with the tensile tests, the fibers showing the largest increase in E' also showed the greatest ultimate strength.

The imaginary modulus (E'') showed little in the way of a trend. Both substantial increases and decreases in E'' were measured with no discernable trend

TABLE III
DMA Results: Properties of Different LMFR and HMFR-PP Fibers with and Without CNTs

	E' (10^9 dyn/cm ²)				E'' (10^9 dyn/cm ²)			
	-50°C	0°C	25°C	75°C	-50°C	0°C	25°C	75°C
LMFR PP								
As-spun neat	58.2	16.2	9.13	3.88	2.87	2.45	1.01	.698
As-spun 1% CNT	73.8	40.0	20.9	7.47	2.70	4.04	1.78	1.00
Change with CNT (%)	26.8	147	129	92.5	-5.93	64.9	76.2	43.3
Postdrawn neat	150	123	101	63.2	6.37	4.12	4.43	5.38
Postdrawn 1% CNT	213	141	109	56.2	8.57	8.21	4.33	5.98
Change with CNT (%)	42.0	14.6	7.92	-10.8	34.5	99.3	-2.3	11.2
HMFR PP								
As-spun neat	42.4	22.3	14.7	5.55	2.79	2.08	1.24	.797
As-spun 1% CNT	69.5	50.8	33.5	9.97	1.43	1.87	1.85	1.24
Change with CNT (%)	63.9	127	127	79.6	-48.7	-10.1	52.9	55.6
Postdrawn neat	131	104	88.6	54.2	6.15	4.27	3.52	5.08
Postdrawn 1% CNT	146	109	86.9	41.4	6.37	4.12	4.43	5.05
Change with CNT (%)	11.5	4.8	-1.9	-23.6	3.58	-3.51	25.9	-0.05

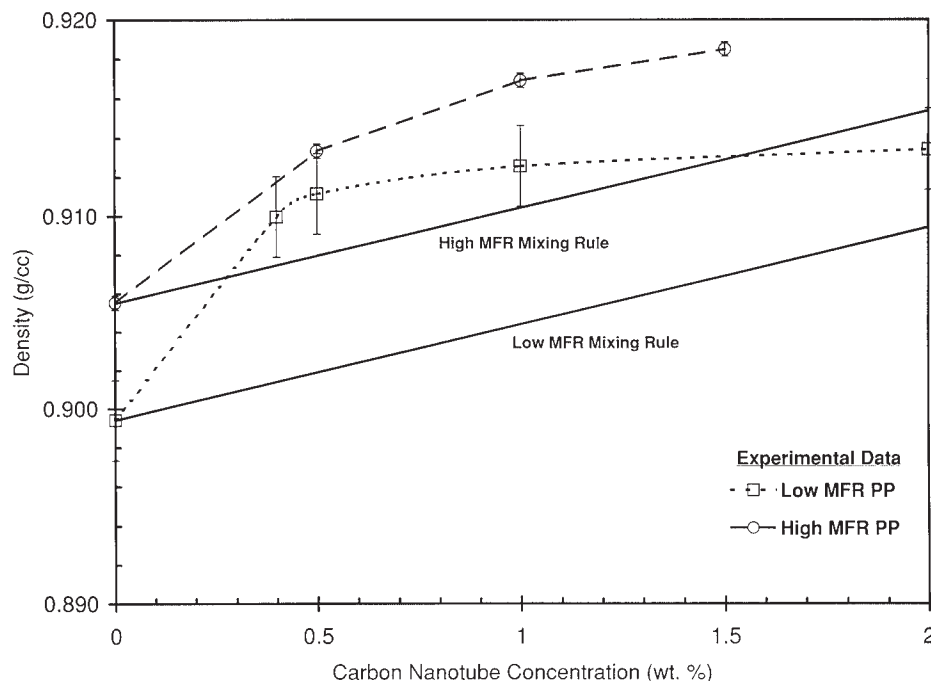


Figure 6 Density of PP extrudates at room temperature as a function of CNT concentration. The linear mixing rule was used with an assumed CNT density of 1.40 g/cc.

or relationship related to either polymer grade or nanotube loading.

Composite density

Density measurements of the CNT/PP extrudate showed strong nonlinear behavior that was indicative of polymer–nanotube interactions. As shown in Figure 6, the addition of even minute quantities of CNTs to PP had a relatively large effect on the overall density. As a first approximation, it was assumed that the following mixing rule applied to the density of the nanotube-reinforced polymer fibers:

$$\rho_{\text{Theoretical}} = \alpha \cdot \rho_{\text{CNT}} + (1 - \alpha) \cdot \rho_{\text{PP}} \quad (2)$$

where α is the mass fraction of CNTs; $\rho_{\text{Theoretical}}$ is the theoretical density of the composite; ρ_{CNT} is the density of bulk CNTs, assumed to be 1.40 g/cm³; and ρ_{PP} is the density of neat PP.

Equation (2) assumes that the density of the composite is linearly related to the mass fraction of each component. [Kearns and Shambaugh⁸ assumed that a mixing rule similar to eq. (2) could be applied to fiber tenacity.] For 100% CNTs, it was assumed that the bulk density was 1.40 g/cm³. Equation (2) is a linear simplification of a complex phenomenon. For example, the equation does not consider any positive, synergistic effects (or any negative effects either) that the nanotubes may have on polymer crystallization or

orientation. However, as a first attempt, the equation is useful.

Equation (2) assumes that the density of the composite is linearly related to the mass fraction of each component, which in turn, assumes that nanotubes do not effect either polymer crystallization or densification effects due to orientation. Clearly, eq. (2) underpredicts the composite fiber densities. The most likely explanation for this nonlinear behavior is the nucleation of crystallization in the PP by the CNTs, as shown by Grady et al.¹² If nucleation leads to higher crystallinities, crystallization is probably limited by the cooling rate of the material; that is, the cooling rate is fast enough so that the material does not have time to crystallize. The nonlinearity of the density plots seemed unrelated to the grade of PP studied. Both the LMFR and HMFR samples showed the same basic nonlinear shape. The graphs of these two materials had slightly different starting densities because of the different fractional crystallinities of the neat materials.

CONCLUSIONS

Conventional tensile testing showed that different grades of PP responded differently to the addition of CNTs. The neat, higher viscosity grade (LMFR) material yielded an as-spun fiber with a tenacity of approximately 1.5 g/denier and a postdrawn strength of over 9 g/denier. The neat, lower viscosity grade (HMFR) PP gave as-spun and postdrawn strengths of 0.9 and 7

g/denier, respectively. The LMFR material showed increases in strength in the postdrawn fibers with compositions as high as 1% CNTs. However, the HMFR showed decreases in strength at all concentrations.

For both HMFR and LMFR materials at lower temperatures, E' increased with the addition of CNTs. For both HMFR and LMFR materials, E'' was not a significant function of nanotube concentration.

Fiber density was a nonlinear function of nanotube concentration. For both LMFR and HMFR materials, the density increases exceeded the densities predicted from a simple linear model.

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