

Polypropylene Fibers Reinforced with Carbon Nanotubes

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ABSTRACT: The strength properties of polypropylene fibers were enhanced with single-wall carbon nanotubes (SWNTs). Solvent processing was used to disperse SWNTs in a commodity polypropylene. After the solvent was removed, the solid polymer was melt-spun and postdrawn into fibers of unusual strength. For a 1-wt % loading of nanotubes, the fiber tensile strength increased 40% (from 9.0

to 13.1 g/denier). At the same time, the modulus increased 55% (from 60 to 93 g/denier). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2079–2084, 2002

Key words: fibers; poly(propylene)(PP); nanocomposite; processing; modulus

INTRODUCTION

For sheets and films, a number of investigators have used nanotubes as the reinforcement in a nanotube/polymer composite. For example, Schadler et al.¹ and Gong et al.² produced composites of nanotubes in epoxy. Shaffer and Windle³ examined a nanotube/poly(vinyl alcohol) composite. Bower et al.⁴ fabricated a composite with nanotubes in polyhydroxyaminoether. Unless sheets and films are unusually thin, they can also be reinforced with more normally sized (e.g., diameters of 100 microns or more) reinforcement. However, nanoscale reinforcement is uniquely suited for strengthening polymer fibers, since the fibers themselves are typically only 10–100 microns in diameter. Since nanotubes are orders of magnitude smaller in diameter, a nanotube cannot occlude a high fraction of the fiber cross section.

Presently, fibers produced from “commodity” polymers (e.g., polyester, polypropylene, and nylon) have tensile strengths from about 0.15 to 0.6 GPa. More expensive “specialty” fibers (such as Kevlar® and PAN carbon fiber) have strengths of about 2–5 GPa. The recently discovered carbon nanotubes have a theoretical strength of 200 GPa (Schadler et al.¹)—about 40 times higher than that of existing materials. However, capitalizing on this potential strength has thus far been problematic.

Several research teams have used single-wall carbon nanotubes (SWNTs) to enhance the strength of neat fibers. Andrews et al.⁵ dispersed SWNTs in isotropic petroleum pitch. With a 5-wt % loading, the tensile strength and modulus were increased 90 and 150%, respectively. Haggemueller et al.⁶ reinforced poly(methyl methacrylate) (PMMA) with SWNTs. They found a

54% increase in the tensile strength and a 94% increase in the modulus when an 8-wt % loading of nanotubes was used.

NANOTUBE DISPERSION AND ADHESION

Nanotube dispersion in the matrix and nanotube adhesion to the matrix are critical to capitalizing on the strength of the nanotubes. The dispersion is interrelated to the form in which the nanotubes are produced. For example, if nanotubes are produced via heterogeneous catalysis, the nanotubes may contain catalyst particles and silica support. It may be possible to use the impure tubes or it may be necessary to purify the nanotubes. For example, a caustic treatment could be used to remove the silica, and then an acid treatment could be used to remove the catalyst metal. Furthermore, an attempt may be made to separate the SWNTs from the multiple-wall nanotubes (MWNTs). Besides mineral acids and bases, organic surfactants may be used in these purification steps.

Most MWNTs are believed to have a “Russian doll” structure, where only weak van de Waal forces bond one tube to another.⁷ Hence, the outer layers of an MWNT could slide or telescope relative to each other.^{1,3} However, kinks and defects could help prevent this sliding.⁷ Ruoff and Lorents⁸ believed that SWNTs are preferable to MWNTs because SWNTs are easier to bond than are MWNTs. These researchers also felt that the tensile strength of the modified SWNTs might be affected by bonding. However, Garg and Sinnott⁹ (also see Harris⁷) showed, in theoretical calculations, that covalent attachments only decrease SWNT strength by about 15%.

Carboxyl® AP-grade nanotubes are a type of commercially available nanotube material. Carboxyl® AP-grade nanotubes are an “as-prepared” nanotube ma-

terial that contains about 70% SWNT and is produced by a carbon arc process. Previous investigators have used ultrasonic mixing¹ or mechanical mixing and a surfactant³ to disperse material of this type. However, both of these investigator teams reported that dispersion was not uniform and that further work was needed. With the unique size range of nanotubes, the phase behavior of nanotubes in polymers will probably affect their dispersion. For submicron particles, phase-separation processes occur which are not observed in macroscopic (micron-scale) systems. In particular, colloidal crystals are produced which depend on the form of interparticle forces.¹⁰⁻¹²

NANOTUBE ORIENTATION DURING FIBER SPINNING

In the fiber-spinning process, high stress during spinning and drawing can result in orientation of the crystal zones in the fiber¹³; the result is a high-strength fiber. Since nanotubes are of similar size to the crystallites, the nanotubes will probably orient in a manner similar to the crystallites. Furthermore, the nanotubes may act as crystallite seeds. Because the nanotubes have such a large surface area per volume, then, even with a small percentage of nanotubes, a large fraction of the polymer matrix could be in close proximity to a nanotube surface.

Melt spinning involves polymers that are melt-processible (thermoplastic). The polymer is melted, pressurized, and forced through a fine capillary. The fiber can be drawn down with either a mechanical roll (with speeds up to 10,000 m/min) or with air jets (with speeds to 30,000 m/min). If the air jets are placed in the melt die, this process is called melt blowing. The speeds possible with melt spinning are orders of magnitude higher than are the speeds used in solution spinning. Hence, melt spinning is an inherently less expensive process for producing fibers. If nanotubes are added to thermoplastic fibers (e.g., polypropylene and polyester), unusually high strengths may result.

EXPERIMENTAL

Dispersion of nanotubes in the polymer

Solvents can be used to produce a uniform dispersion of nanotubes in a thermoplastic polymer. Then, the solvents can be removed and the polymer can be processed via inexpensive melt spinning. For example, the nanotubes can first be dispersed in a suitable solvent. Mechanical mixing, sonification, a surfactant, and other means may be necessary to accomplish this task. Next, thermoplastic pellets are added to the mixture and further mixing and heating are done. Finally, the resulting mixture is dried. The drying process consists of drying at room temperature and/or ele-

vated temperatures. Also, drying at atmospheric pressure and/or reduced pressure (vacuum) can be used. The final dried material will contain roughly 1% solvent or less; the remaining solvent will act as a plasticizer.

If several solvents are used (versus a single solvent), then the solvents probably need some level of mutual solubility. Similarly, if one or more surfactants are used, then these surfactants must positively interact with each other and with the other components (solvents, nanotubes, and polymer).

After the solvent(s) is removed from the polymer, the resultant material can be crushed into a coarse material (chunks that are 0.5 cm across or less should be adequate). Then, this solid material can be melt-spun as would an ordinary meltable polymer. Spinning speeds should be in the range typical for melt spinning.

As has been discussed in the literature, the dissolution of SWNTs in organic solvents is not well understood at the present time.¹⁴ However, a long-term (stable) suspension may not be necessary for the success of the process. A good, temporary dispersion may be all that is required, since, once the polymer is added, the material thickens greatly and the chances of nanotube clumping are greatly reduced.

Experiments with polypropylene

Nanotubes were added to a commodity polypropylene (PP). Fina Dypro[®] isotactic PP pellets were used for all experiments. The polymer had an MFR of 88, an M_w of 165,000 g/mol, and a polydispersity of 4. A common decahydronaphthalene (decalin) solvent was used. This solvent is known to dissolve PP. The nanotubes used were Carboxex[®] AP-grade SWNTs. These tubes are about 50–70% (by volume) SWNTs. The Carboxex[®] material was not purified. Purification can be a lengthy, expensive process. Hence, as a first step, it was felt that unpurified material should be tested.

Typically, the experiments were begun by placing 150 mL of decalin in a 400-mL beaker. Next, the appropriate amount of Carboxex[®] nanotubes were added to the decalin. Then, the mixture was sonicated with a Fisher Scientific Model 550 ultrasonic generator. While the sonification took place, the mixture was heated due to the effect of sonification. Next, the beaker was placed on a hot plate and PP pellets were added to the mixture. Sonification was continued, and the temperature was brought to 135°C by adding thermal energy from the hot plate.

After the appropriate heating and mixing time (typically 2 h), the hot beaker of the solution was placed in a vacuum oven set at a temperature of 70°C and an absolute pressure of 10.1 kPa. After (typically) 2 days, the beaker was removed from the vacuum oven. The

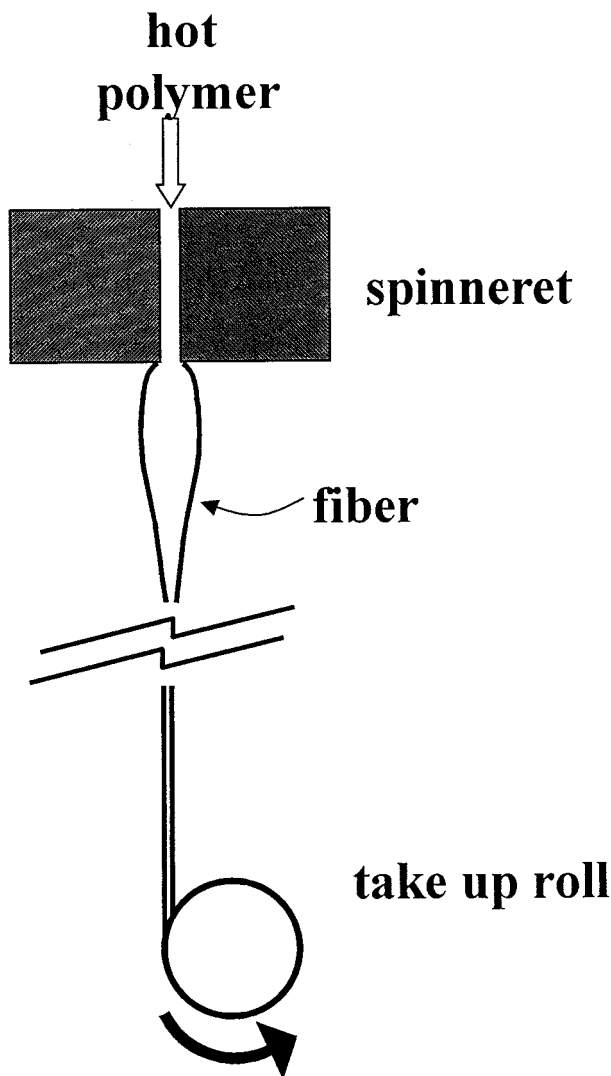


Figure 1 The melt-spinning process.

resultant dried material was a coarse powder (the chunks were all 0.5-cm size and less). The powder was weighed, and these weight measurements showed that the final material had less than 1 wt % of decalin remaining.

The dried polymer was placed in an extruder (see Fig. 1). The material was then heated to 190°C and the polymer was extruded out at a mass rate of 0.50 g/min. The spinneret had a 1.22-mm hole and an L/D of 5. A 15.2-cm diameter mechanical roll was placed at a distance of 1.35 m below the spinneret. The roll was run at a surface speed of 519 m/min, and the fiber was collected on the roll. The collected fiber was then postdrawn by passing the fiber through an oven set at 125°C. The oven length was 38 cm, the feed roll (6.5-cm diameter) was run at a surface speed of 1.5 m/min, and the take-up roll (also 6.5-cm diameter) was run at a higher surface speed that was determined by the desired draw ratio.

The drawn fiber was tested with an Instron tensile test machine at a strain rate of 2.54 cm/min and with a sample length of 2.29 cm. Fiber diameters were determined with a Nikon Labophot2-Pol microscope and a micrometer eyepiece.

RESULTS AND DISCUSSION

Figure 2 compares the stress-strain behavior of neat PP fibers with PP fibers containing 1 wt % nanotubes. The neat PP fibers are labeled "PP-D" to indicate that the fibers have gone through the decalin processing with 0% nanotube addition. Similarly, the nanotube-containing fibers are labeled "PP-D-1% CNT." The addition level is based on the weight of impure Carbolex® material—that is, the actual level of SWNTs is less than 1%. The fibers shown in Figure 2 were all processed with 1 h of sonification of the nanotube-decalin mixture. Then, the PP pellets were added, heat was input from the hot plate (until 135°C was reached), and sonification was continued for another hour. The sonicator had a 1.27-cm (0.5-in.) diameter titanium tip and was operated at 20 kHz. The sonicator power setting was "4." By thermal loss measurements,¹⁵ it was determined that this setting corresponded to a power input of 24 W.

In Figure 2 are shown five replicate tensile tests for both the PP-D sample and the PP-D-1% CNT sample. The average tensile strength for the PP-D was 9.0 g/den, while the average tensile strength was 13.1 g/den for the PP-D-1% CNT. This is a very significant increase of 40%. Similarly, the modulus (at 4% elongation) of the PP-D-1% CNT is 55% higher than is the modulus of the PP-D fiber (93 g/den versus 60 g/den).

A fiber with 0.5% nanotubes (PP-D-0.5% CNT) was prepared according to the same procedure used to

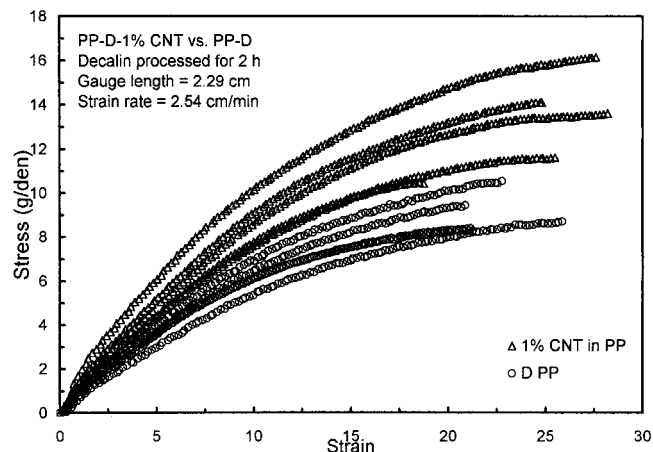


Figure 2 Replicate stress-strain curves of PP-D fibers and PP-D-1% CNT fibers postdrawn at 125°C to a diameter of 15 μ m and the maximum possible draw ratio (8.3 for PP-D-1% CNT; 9.3 for PP-D).

TABLE I
Fiber Strengths as a Function of Nanotube Loading

Researchers	Fiber type	Density (g/cm ³)	% CNT loading	Tensile strength		E_b^d	Modulus ^e		Tenacity		
				psi	MPa		psi	GPa	dN/tex	g/den	
Andrews et al.	Isotropic pitch	1.24 ^a	0	69,600	480		4,930,000	34	3.87	4.4	
			1	88,500	610		1.25	5,950,000	41	4.92	5.6
			5	130,600	900		1.35	11,240,000	78	7.26	8.2
Haggen-mueller et al.	PMMA	1.19 ^b	0	12,600	87		450,000	3.1	0.73	0.83	
			1	17,100	117		479,000	3.3	0.99	1.1	
			5	18,000	124		725,000	5	1.04	1.2	
			8	19,600	134		870,000	6	1.14	1.3	
This work	PP	0.895 ^c	0	102,800	709	18.9	913,000	6.3	7.93	9.0	
			0.5	121,600	838		19.1	1,350,000	9.3	9.37	10.6
			1	149,700	1032		26.6	1,420,000	9.8	11.5	13.1

^a Ref. 16.

^b Ref. 17.

^c Ref. 18.

^d Percent elongation at break.

^e Measured at 4% elongation for this work; not specified in the other works.

produce the 1% nanotube fibers. The tenacity and modulus of these fibers were intermediate between the neat (0%) fibers and the 1% nanotube fibers (see Table I). Nanotube loadings of 1.5 and 2% were also attempted. However, at these loadings, spinning was difficult, and the tensile properties were lower than were the properties of neat PP. Perhaps the impurities in the Carbolex[®] become too great a problem at these higher nanotube loadings. High impurity levels may cause localized occlusion of a significant fraction of the fiber diameter. This would account for both poor spinning and poor tensile properties.

A strength of 9.0 g/den is typical of high-strength industrial PP fibers. For our PP-D samples, a maximum draw ratio of 9.3 was used to achieve this strength. For comparison, PP fibers were also produced (with no decalin processing). These samples required a slightly lower draw ratio (8.9 for PP versus 9.3 for PP-D). Plasticization by the residual decalin probably caused this small difference. However, the stress-strain behavior of PP-D fibers is essentially identical to the behavior of PP fibers. The maximum draw ratio for the PP-D-1% CNT fibers was 8.3. This lower value was undoubtedly due to the stiffening of the fibers caused by the nanotubes.

Effects of sonification time and choice of solvent

As stated above, the results in Figure 2 were produced with 2 h of sonification; this time was split into 1 h before PP was added and 1 h after PP was added. To test the effect of this sonification time, tests were run with total sonification times of 0.5–12 h. These times were split 50:50 between the time before polymer addition and the time after polymer addition. Figure 3 shows the results of these tests for PP-D-1% CNT

fibers. As can be seen, the best result occurred with the 2-h sonification time. Lower times probably gave inadequate mixing and dispersion of the nanotubes and polymer. Higher times probably resulted in nanotube breakage and damage. Each stress-strain curve in Figure 3 is the average of five replicate measurements.

In the literature, a number of investigators discussed the use of toluene to disperse nanotubes.^{19,20} In fact, nanotubes are sometimes sold as a dispersion in toluene. Guided by this information, nanotubes were first dispersed in toluene with sonification. Separately, PP was dissolved in decalin (toluene is not a good solvent for PP). Then, the two solvents were mixed, heated to 135°C, and sonicated. Except for the use of two solvents, the procedure was essentially the same as that used for the single-solvent (decalin) process.

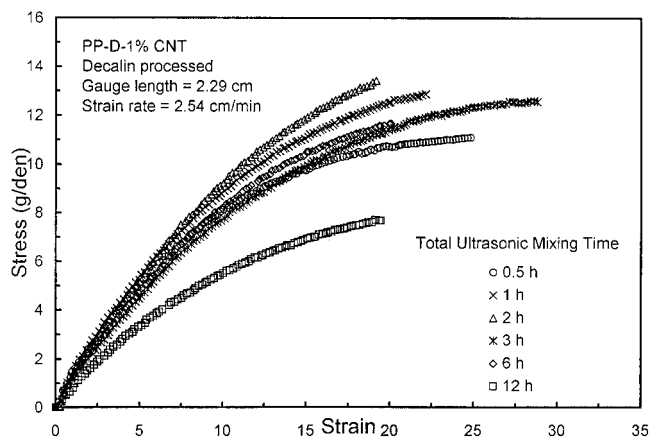


Figure 3 Effect of ultrasonic mixing time on the fiber strength. Each curve is the average of five replicate tensile tests. The maximum draw ratios were used for each mixing time. These ratios were 7.9 for 0.5 h, 7.6 for 1 h, 8.3 for 2 h, 8.6 for 6 h, and 7.2 for 12 h.

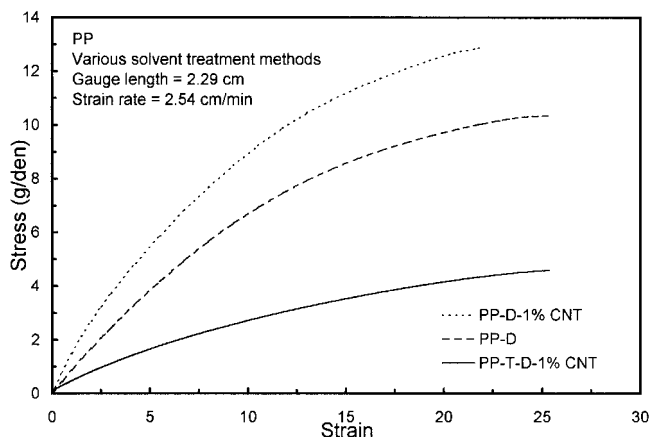


Figure 4 Typical stress–strain curves of 1% CNTs in solvent-processed PP fibers postdrawn at 110°C to the maximum possible draw ratio (8.3 for PP-D-1% CNT, 9.3 for PP-D, 6.0 for PP-T-D-1% CNT).

Then, the material was dried, spun, postdrawn, and tensile-tested. Since decalin and toluene are mutually soluble in all proportions, it was hoped that this mixed solvent technique might produce improved dispersion and, consequently, improved fiber properties. Figure 4 shows the results of this test. The toluene sample (PP-T-D-1% CNT) is compared to PP-D and PP-D-1% CNT. Each curve represents the average of five replicate tensile tests. As can be seen, the use of the toluene–decalin mixed solvent system did not produce good results.

Actual strength versus theoretical strength

As was previously mentioned, Table I shows the tensile strength and modulus of our PP fibers with nanotube loadings of 0, 0.5, and 1%. These properties increase as nanotube loading increases. Also shown in the table are fiber results from two other groups of researchers. Similar to our results, these researchers showed that fiber tensile properties increased when nanotubes were added to a polymer.

Can we quantify how effective the nanotubes are in reinforcing the polymer fibers shown in Table 1? As a first approximation, it was assumed that the following mixing rule applies to the strength of nanotube-reinforced polymer fibers:

$$S = (1 - x)S_p + xS_n \quad (1)$$

where S is the tenacity of the nanotube-reinforced fiber; S_p , the tenacity of the neat polymer fiber; S_n , the tenacity of the neat nanotube fiber; and x , the weight fraction of the nanotubes in polymer.

Measured values were used for S_p , while S_n was assumed to be 1373 g/den [based on a tenacity of 200 GPa (Schadler et al.¹) and a nanotube density of 1.65 g/cm³

(Shaffer et al.²¹)]. Equation (1) is a linear simplification of a complex phenomenon. For example, the equation does not take into account any positive, synergistic effects that the nanotubes may have on polymer crystallization or orientation (or any negative effects either). However, as a first attempt, the equation is useful.

The tensile strengths listed in Table I are plotted in Figure 5. Also in Figure 5 are the theoretical fiber strengths that were predicted based on eq. (1). The neat PP fibers are stronger than either the PMMA or the petroleum pitch fibers. As nanotubes are added, the PP and pitch fibers appear to better utilize the nanotubes than does the PMMA material. Figure 6 quantifies this utilization by plotting the percent of theoretical strength versus the percent nanotubes. The percent of theoretical strength is simply the measured fiber strength divided by the theoretical strength determined by eq. (1). Thus, at a 1% loading of nanotubes, Figure 6 shows that PP/CNT is about 58% effective, pitch/CNT is about 32% effective, and PMMA/CNT is about 7% effective. Apparently, PP fibers are very amenable to the reinforcing effect of nanotubes.

CONCLUSIONS

Unpurified SWNTs were used to reinforce PP fibers at nanotube loading levels up to 1 wt percent. With a combination of solvent processing and melt spinning, the SWNTs were very effectively utilized in strengthening the PP fibers. At a 1% loading level, the fibers had tensile strengths that were intermediate between high-strength industrial PP and Kevlar® fibers.

NOMENCLATURE

MFR melt-flow rate
 M_w weight-average molecular weight (g/mol)

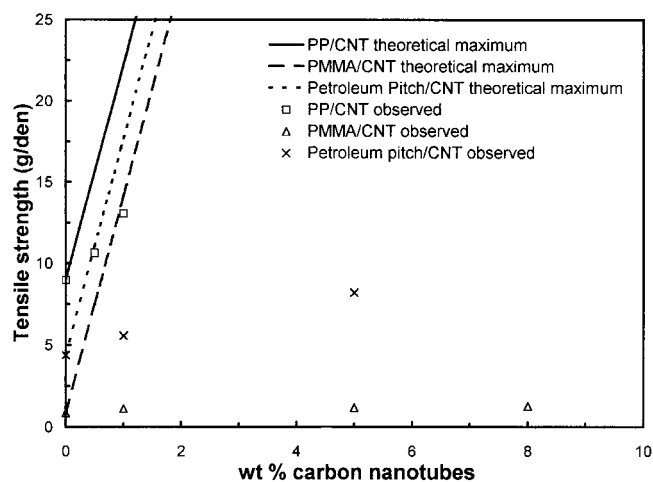


Figure 5 Observed tensile strengths versus theoretical tensile strengths.

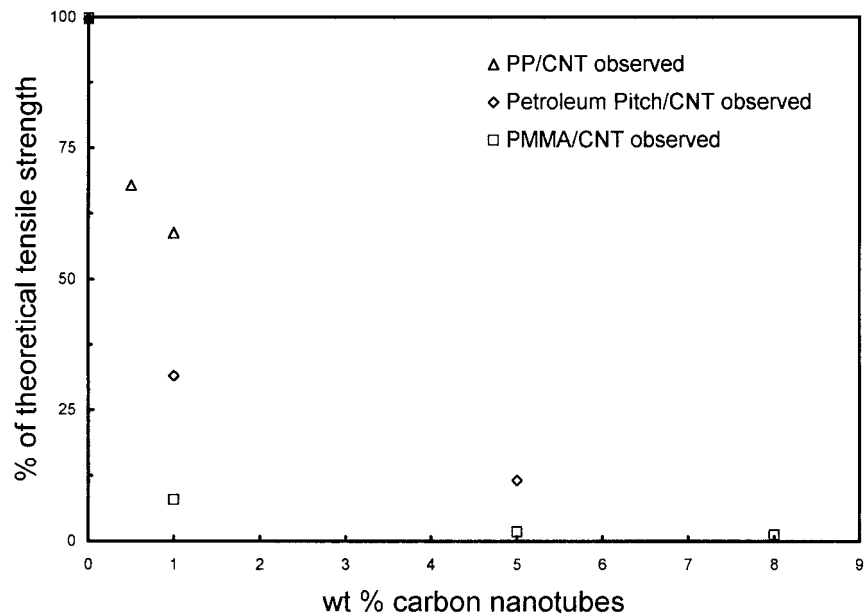


Figure 6 Observed tensile strength as a percentage of the theoretical maximum as determined by the mixing rule.

S tenacity of nanotube-reinforced fiber (g/den)
 S_p tenacity of neat polymer fiber (g/den)
 S_n tenacity of neat nanotube fiber (g/den)
 x weight fraction of nanotubes in polymer

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