

Silica Supported Single-Walled Carbon Nanotubes as a Modifier in Polyethylene Composites

Neal D. McDaniel, Max P. McDaniel, Leandro Balzano, Daniel E. Resasco

School of Chemical, Biological, and Materials Engineering, University of Oklahoma, Norman, Oklahoma

Received 5 June 2008; accepted 9 June 2008

DOI 10.1002/app.28916

Published online 10 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Composites have been made from single-wall carbon nanotubes in a polyethylene (PE) matrix, in which different methods of preparation were used to disperse the nanotubes. The study includes using either the refined pure nanotubes (P-NT) as the source, or the original silica supported nanotubes (SS-NT). SS-NT contained nanotubes still incorporated in and around the silica as originally grown. Composites were then made by (1) coprecipitation from a suspension of P-NT or SS-NT in a PE solution, or (2) by forming a polymerization catalyst from the SS-NT, and using it to polymerize ethylene, which ruptures and expands the silica as polymer builds up in the pores. Extrusion was also studied as a method of additional dispersion. Nanotubes were found to have a powerful effect on the melt rheology, increasing the low shear viscosity dramatically. Increasing the nanotube

concentration also increased the flexural and tensile moduli, decreased the elongation, and increased the electrical conductivity. Consistent trends were observed from all of these diverse properties: SS-NT had a stronger effect than P-NT, and within the SS-NT group the choice of silica type also had a major effect. Polymerization was generally preferred as the method of dispersing the nanotubes. The conductivity, which in some cases was quite high, was found to be pressure sensitive. Conductive NT/PE composites could be molded into films or extruded into other shapes, or comolded with other PE. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 589–601, 2009

Key words: additives; composites; conducting polymers; nanocomposites; polyethylene

INTRODUCTION

Polyethylene (PE) is the most widely used plastic because it is least costly, easily molded by many different processes, and exhibits a wide variety of useful properties such as high chemical, electrical, and impact resistance.¹ The properties of PE are sometimes further modified by adding inorganic reinforcing agents, such as calcium carbonate, clay, talc, mica, powdered metals, and carbon black. Such fillers usually increase stiffness and diffusional barrier performance, block light transmission, and the latter two are sometimes added to generate electrical conductivity. The development of carbon nanotubes (NT) in recent years offers a potentially powerful new form of filler due to its extreme aspect ratio.^{2–5} These new materials are also highly conductive, which makes them attractive for applications in chemical storage, fuel tanks, drums, and other functions that require grounding.

A major problem associated with blending fillers into molten PE is the difficulty of dispersing the individual particles into the polymer matrix. Indeed,

the quality of dispersion turns out to be the critical variable when designing such composites. High shear extrusion mixing is usually employed for this purpose. The carbon NT are especially problematic in this respect because they are only a few angstroms in diameter, as opposed to microns for other materials.⁶ To take full advantage of their high aspect ratio, they must be dispersed at the nanometer level. However, they have a much stronger Van der Waals affinity for each other than they have for the PE matrix. This makes it especially hard to break up clusters of NT, effectively disperse them, and keep them dispersed in the polymer.

To accomplish such dispersal, several experimental methods have been tested in this study using single-walled NT. In addition to extrusion blending the NT into molten polymer, NT was also dispersed by sonication into solutions of PE, followed by “quenching,” i.e., fast coprecipitation in cold alcohol. In another approach, the polymerization mechanism itself was tested as a means of dispersing the NT. NT was first made on Co/silica catalyst, which was then converted into a polymerization catalyst and allowed to polymerize ethylene. It is a well-known feature of ethylene polymerization that the pores of each catalyst particle quickly fill with polymer and then rupture as more polymer is produced, fracturing each silica particle into a billion smaller

Correspondence to: Neal D. McDaniel (nmcdanie@princeton.edu).

fragments of $\leq 0.1 \mu\text{m}$.^{7,8} Each fragment becomes surrounded in a coating of polymer that moves away from its neighbors in an expanding larger mass. Often called the "multi-grain" model of particle fragmentation and growth,⁷ it was hoped that accompanying NT might become intimately dispersed in the PE made during this process.

Several recent publications have attempted to use *in situ* polymer formation as a way of making NT-PE composites. DuBois and coworkers tried to coat refined multi-walled NT with metallocene/MAO catalyst components, followed by very low-yield ethylene polymerization.⁹⁻¹¹ They reported that this process produced NT/PE mixtures that were more effectively blended into PE by subsequent extrusion mixing. Similarly, Tong et al. attempted to coat single-walled NT with Ziegler catalyst components.¹² Again PE was generated at low yield and this material was then extrusion blended into PE. *In situ* polymerization yielded a source of NT that was found to be more compatible with PE. Improvements in physical properties of PE were reported. This report is another attempt to produce superior dispersion in PE by *in situ* polymerization. However, unlike previous reports that incorporated refined and isolated NT, which exists in agglomerated bundles, the present study instead used the original silica-supported NT in its nascent form. *In situ* PE was then generated, not as a compatibilizer for extrusion mixing with other PE, but to make the final NT/PE composite.

EXPERIMENTAL

Carbon nanotube preparation

Silica-supported single-wall carbon NT were generated via carbon monoxide disproportionation on Co-Mo/SiO₂ catalyst. This method is referred to as CoMoCAT, and has been previously described.¹³⁻¹⁶ This process yields materials of narrow distribution of diameters and chiralities, comprised mostly of (6,5) and (7,5) types.¹⁷⁻¹⁹ After impregnation of the silica support with cobalt nitrate and ammonium heptamolybdate, the resultant catalyst was calcined at 500°C for 1 h in dry air, then reduced with H₂ at 500°C for 30 min, followed by exposure to flowing CO at 750°C for 2 h to produce the NT. The final result of this process was a black powder containing from 2 to 8 wt % carbon. This material is referred to below as "silica-supported nanotubes" or just "SS-NT." For comparison, analogous materials to those described above were purified of their inert silica supports by ultrasonic agitation in hydrofluoric acid, followed by extensive dilution with H₂O. High energy ultrasound was used to separate the tubes, which have a natural affinity for one another. Surfac-

tants and freeze-drying help prevent the NT from bundling into rope-like secondary structures. The finished material is referred to below as pure NT, or "P-NT."

Silicas

Three grades of commercial silica, which varied widely in their physical characteristics, were chosen for this study. These three silicas represent a broad diversity in structure, formed by high pH precipitation, low pH gelation, and vaporized flame hydrolysis. Hisil 210 is a precipitated silica obtained from Pittsburg Plate Glass Co. having a BET surface area of 135 m²/g and containing 1% NaCl. It was sold as a pellet, which was ground to a particle size of 100–200 μm before use in this study. Syloid 244 is a gelled silica obtained from W.R. Grace Co. having a surface area of 300 m²/g, a pore volume of 1.5 cc/g, an average particle size of 3–7 μm , and containing <0.1% Na₂O. Cabosil EH-5 is a flame hydrolyzed silica obtained from Cabot Corp., consisting of 7 nm primary particles fused into 200 nm chains. Agglomerates of up to 25 μm can be formed upon handling, but they are held together only by chain entanglements and hydrogen bonding, and are easily broken up by stirring and sonication. This material has a surface area of 400 m²/g but is not considered as having a pore structure.

Methods of dispersing NT

Four different methods of NT dispersion into a PE matrix were employed for comparison. These are described below.

Extrusion mixing PE and NT

Mechanical mixing of PE (>99.5% from Chevron-Phillips Co.) and SS-NT was accomplished using a DACA Microcompounder twin-screw extruder. Composites were prepared by extrusion mixing at 220°C for 15 min. These blends are referred to with the "A" prefix.

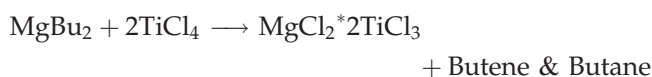
Coprecipitating PE and NT

PE was dissolved at 120–140°C in trichlorobenzene (TCB). To this solution P-NT or SS-NT was added, according to the experiment. In cases where P-NT was used, the resultant suspension was subjected to high energy ultrasonication for 10 min. However, sonication was not performed on samples that employed SS-NT, to preserve the original secondary structure of the supported NT. For both pure and supported NT, the resulting mixture was then quickly added to a large excess of 2-propanol,

causing the instantaneous coprecipitation of PE and NT. The slurry was then filtered to separate the dark solid from the now colorless solvent mixture. Final rinsing with acetone removed residual TCB, after which the composite material was dried under vacuum at 60°C. Composites made by this method are designated with the "B" prefix.

Dispersing NT via polymerization

To prepare a polymerization catalyst the SS-NT was first heated to 300–400°C in nitrogen to remove moisture picked up during handling. Either P-NT or SS-NT, depending on the individual experiment, was converted into a Ziegler catalyst by impregnation with dibutylmagnesium in heptane followed by TiCl₄.



A low loading, 0.1–0.2 mmol of Mg was added per gram SS-NT, so that all the Mg, would be adsorbed. To this slurry was then added 1–2 equivalents of TiCl₄.²⁰ In this way the catalyst is formed within the pores of the silica. P-NT samples were impregnated/coated with dibutylmagnesium in heptane, which was then evaporated to dryness. Afterward the sample was exposed to TiCl₄ vapor to avoid dissolving the Mg again. These catalysts were then used to polymerize ethylene in a process that is known to disintegrate the support into small fragments.⁸ These composites are designated by the "C" prefix.

Immobilizing P-NT in an oxide gel

P-NT were first suspended in an aqueous medium using both ultrasonication and surfactants. To maintain dispersion, the liquid matrix was then gelled by the instantaneous precipitation of an oxide or hydroxide, freezing the NT in place. This metal oxide was in some cases silica, from the *in situ* hydrolysis of Si(OEt)₄, or in other cases magnesia, from the *in situ* formation of Mg(OH)₂ from MgCl₂. The nanotube containing oxide was then used as a carrier to form a polymerization catalyst, as described above. These composites are designated by the "D" prefix.

Ethylene polymerization

Larger-scale polymerizations were conducted in a jacketed 2.2-L steel reactor equipped with electronic temperature control. Typically, from 0.5 to 10 g of catalyst was charged under nitrogen to the dry reactor, then 1.2 L of isobutane liquid, and 2 mL of a 1M triethylaluminum (TEA) solution. H₂ was sometimes added, 15–30 psi on the reactor, to control MW. The

reactor temperature was raised to the specified point, usually 80–100°C, and ethylene was then added to maintain a fixed pressure, usually 300 or 450 psig. After 10–30 min the reactor was depressurized and opened to recover 5–200 g of granular polymer powder.

Smaller polymerizations were performed at about 50°C in a Diels–Alder bottle using dry heptane as solvent. After the addition of catalyst, heptane, and TEA cocatalyst, ethylene was added to maintain 7 psig in the bottle while a magnetic stirring bar kept the slurry agitated. The desired PE yield was reached in 10–60 min and the polymer was removed by filtration. Although the polymerization catalysts' activities were reasonably high, their total production was cut short to achieve the desired NT concentrations in the resulting composites.

Ethylene was polymerization grade obtained from Union Carbide Corp., further purified through alumina. Isobutane was polymerization grade obtained from ConocoPhillips Petroleum Co., further purified by through 13× (10 Å average pore size) molecular sieve.

Polymer characterization

In this article certain well-known rheological parameters have been used in conjunction with independently measured molecular weight distribution to judge the degree of elasticity with and without addition of NT.^{21–23} Samples were stabilized with 0.1 wt % BHT and compression molded into disks of 2 mm × 25.4 mm diameter. Small-strain oscillatory shear measurements were performed on a Rheometrics RMS-800 or ARES rheometer using parallel-plate geometry in which the test chamber was blanketed in nitrogen. On sample loading and after thermal equilibration, specimens were squeezed between the plates to a 1.6 mm thickness. Data were sometimes fitted to the Carreau-Yasuda equation for analysis.^{24–26}

Molecular weights and molecular-weight distributions were obtained from a Waters 150 CV Plus or a Polymer Labs PL220 Gel Permeation Chromatograph using TCB as the solvent with a flow rate of 1 mL/min at a temperature of 140°C. Two Waters Styragel HT 6E mixed-bed columns were used, or three to four PLGel Mixed A columns plus a guard column. A broad-standard integral method of universal calibration was used based on a Phillips Marlex BHB 5003 broad linear PE standard. Parameter values used in the Mark-Houwink equation ($[\eta] = K \cdot Ma^a$) for PE were $K = 39.5$ (10^{–3}) mL/g and $a = 0.726$.

Tensile and elongation measurements were conducted on an Instron 4400 with HRDE extensometer and according to a modified ASTM D638-86 procedure using Type 5 dog-bone tensile bars 0.15 in. × 0.07 in. at the neck × 0.5 in. Crosshead speed was 2.0 in./min.

Flexural modulus measurements (MPa) were conducted on an Instron 4505 at 0.5 in./min using a modified ASTM D790-95a procedure. The modification involved using compression molded slabs measuring 2 in. by 0.5 in. by 0.05 in., and a 1 in. span.

To measure the electrical resistance of NT-PE composites a circular disk of 1.27 cm diameter and 0.13 cm thick was compression molded. To each side of this disk was then smeared a small amount of micronized silver paste. A 1.9 cm diameter brass disk was then pressed against the silver paste on each side of the PE disk, and the two metal plates with sample sandwiched between were then pressed together by means of a spring-loaded clamp. Resistance between these two brass disks was measured with a voltmeter. Conductivity was determined as a function of pressure by placing the composite plaque (5 cm × 5 cm × 0.13 cm) between two brass plates, which were then inserted in a hydraulic press between insulating barriers. Resistance between the plates was then monitored as known amounts of force were applied from the press.

RESULTS AND DISCUSSION

Choice of silica

When converted into polymerization catalysts and exposed to ethylene, the pores of these silicas quickly fill up with PE. At this point the catalyst must fracture into submicron sized fragments to sustain their polymerization activity.^{7,8} Low porosity silicas resist being ruptured by the forces of PE generation, whereas highly porous structures are fragile and are easily broken up. Therefore the structure of silica, characterized by its porosity and surface area, exerts a powerful influence on the activity because it governs the extent of fragmentation. Three grades of commercial silicas were chosen for this study, representing a broad diversity in structure due to different preparation techniques—high pH precipitation, low pH gelation, and vaporized flame hydrolysis.

Hisil 210 does not have the desired high porosity and surface area needed for a successful polymerization catalyst. In addition, the presence of a large amount of sodium on the silica accelerates fusion of primary particles (sintering) during the high temperature calcining steps, further retarding its effectiveness. Therefore, the degree of fragmentation from Hisil-210 is not expected to be high during polymerization. The large size (100–200 μm) of unfragmented Hisil 210 particles can also be detrimental to NT dispersion.

In contrast, the highly porous Syloid 244 and Cabosil EH-5 are both excellent supports for polymerization catalysts. The former has a long history of commercial use in PE manufacture, and both

have high surface area, low sodium, and very small particle size. Some additional weak agglomeration may result when these silicas are impregnated with an aqueous Co/Mo solution and dried. Nevertheless they (and particularly the Cabosil) are thought to represent the finest distribution of small particles that can be easily achieved in the dry state.

NT homogeneity

The macroscopic homogeneity of these PE/NT composites can be assessed by visual inspection of molded thin films. Sheets ranging in thickness from 10 to 70 μm were prepared by pressing the composite between metal plates at 175°C. Lexan film was used to prevent actual contact with the metal plate. This approach detects average differences in nanotube concentration at the millimeter level, but says nothing about dispersion at the submicron level. For example, large agglomerates of P-NT and unfragmented SS-NT (whether individual or an agglomerate) can be observed in a thin film. This characterization tool is especially useful to evaluate the degree of homogeneity in the catalyst. In methods C and D NT-containing materials are converted into polymerization catalysts, which then produce PE. Variations in the film could result from (1) nonuniform impregnation of the Co/Mo solution, (2) nonuniform growth of NT within the bed, (3) nonuniform impregnation of the polymerization ingredients, or (4) nonuniform polymer growth. Depending on the catalyst preparation, inconsistencies between catalyst particles can occur, causing their activity or NT concentration to vary. Because each gram of catalyst produces many grams of PE, this heterogeneity becomes magnified in the polymer, and is sometimes visible in the film.

Blending NT into PE by extrusion (method A) is a well-known dispersion technique, and has been extensively studied.^{2,4,5} Although mechanical mixing produces composites that seem to be homogeneous on a macroscopic scale, the NTs affinity for each other prevents their individual dispersion. Instead, the NT coagulate into microscopic bundles. In this study, an attempt was made to prevent this coagulation by substituting the structured SS-NT for the stereotypical P-NT bundles. This material exhibited the same macroscopic homogeneity as those made from P-NT, although other properties were surprisingly different (discussed below).

Films made from P-NT, added into PE solution by method B, usually looked quite homogeneous. An example of such a film is depicted in Figure 1. However, other observations suggest that these composites were inhomogeneous on a smaller scale. Each of these composites came from refined NT that were first intensely sonicated in TCB. This caused a fine

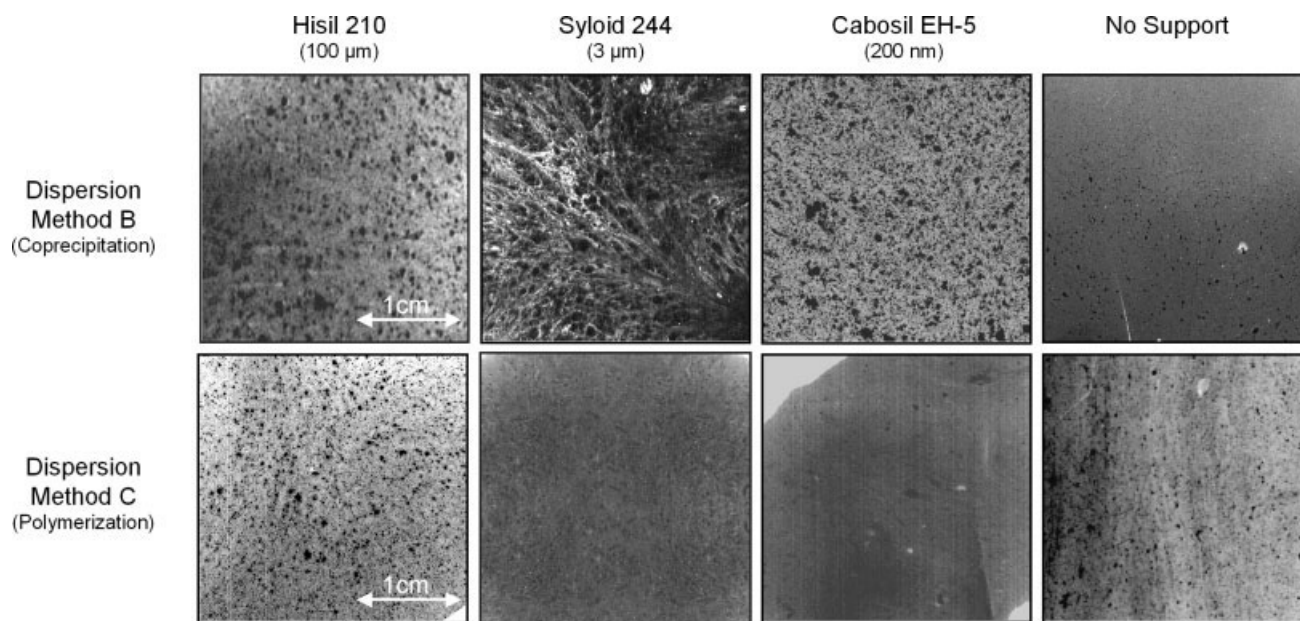


Figure 1 Macroscopic homogeneity of various polymers.

suspension that did not completely settle out even after days at rest. Nevertheless a drop of this suspension, taken immediately from the hot sonicating liquid and placed on a microscope slide, did not have the expected uniform appearance. Instead, one could see a fine microscopic “grainy” structure under magnification. Thus, although the films appeared to be macroscopically uniform, this does not preclude the possibility of microscopic NT clustering.

Composites made by coprecipitation of PE and SS-NT allowed for direct observation of the effect that particle size has on composite homogeneity. Figure 1 depicts three composites made by method B, each from a different grade of silica support. The sample derived from 100 μm Hisil 210 particles has an obvious grainy quality when pressed into a film. Even in the case of finer particles, however, dark patches are apparent. This might be due to aggregates formed during the growth of NT that could not be fully disseminated by sonication, presumably due to the interlocking NT.

Composites made by *in situ* polymerization from a SS-NT support (method C) are also shown in Figure 1. The same three silica carriers were again used. For each silica, composites prepared from method C are more homogenous than their coprecipitated counterparts (method B). This demonstrates a generally superior ability of the polymerization mechanism to disperse the NT, at least on a macroscopic level.

Despite the improved dispersion achieved by method C, differences can still be observed between

the three silicas. Once again, films made from Hisil 210 support have a fine grainy texture, indicating that these particles may not have fragmented. This would be expected from the porosity of this silica, which is not suitable as a support for commercial polymerization catalysts.⁷ On the other hand, Syloid 244 does have the correct porosity for PE manufacture, and is well-known to disintegrate during ethylene polymerization. In addition, this silica starts from a much smaller particle size of 3 μm . Taken together, these facts account for the more uniform appearance of the film, compared with the Hisil 210 sample. Equally homogeneous is the sample prepared from Cabosil EH-5. This silica also has a suitable porosity for ethylene polymerization, in addition to a much smaller particle size of 200 nm.

Method C was also employed in the absence of an inert catalyst support. Purified NT were directly treated with the polymerization catalyst, and then ethylene polymerization produced a composite that was free of inert material. In this case, the resulting film was grainy in appearance, as shown in Figure 1. Despite the obvious macroscopic inhomogeneity of this polymer, compared with its coprecipitated analog above it in Figure 1, other characterization methods suggest that the NT were actually better dispersed. This sample’s grainy macroscopic texture is likely a result of unadsorbed polymerization catalyst. That is, the purified nanotube bundles possess very little porosity in comparison with the silica supports. Unlike the silicas, when purified NT are impregnated with catalyst ingredients, only a portion of that catalyst can be adsorbed on or within

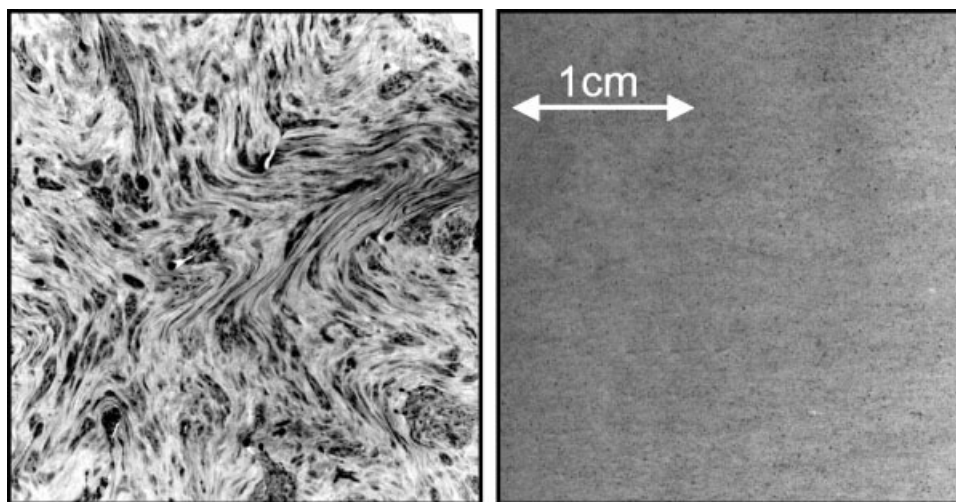


Figure 2 PE composites made from metal oxide supports gelled around suspended nanotubes (left, MgO; right, SiO₂).

the nanotube bundles. The rest of the catalyst is formed independently of the NT, and produces polymer without NT. Therefore, while a fraction of the PE forms between the NT and aids in their dispersion, the rest forms in its own domain, accounting for the patchy appearance of the film.

Macroscopic homogeneity varied widely among composites made by method D, i.e., fabricated from supports that were gelled around surfactant-suspended NT. In one instance, P-NT was suspended by high-power sonication in an aqueous solution containing *n*-methylpyrrolidone and MgCl₂. The NT-containing magnesia matrix was formed by addition of NH₄OH. Mg(OH)₂ was then dehydrated into MgO and converted into a polymerization catalyst by exposure to TiCl₄. The resulting PE composite, shown in the left side of Figure 2, was spotted with millimeter-scale dark patches, a clear indication of nonuniformity in the NT-containing polymerization catalyst. In a similar experiment, the magnesia was removed from the finished composite by washing with dilute hydrochloric acid. This had no effect on the uniformity or other measured properties of the resins.

In yet another experiment, a catalyst was generated from NT immobilized in a silica matrix. P-NT was suspended via high-energy sonication in an aqueous sodium dodecylbenzene sulfonate solution. To this solution was added a silica sol, formed by acidic hydrolysis of ethyl silicate in ethanol. Gelation was achieved by raising the pH with ammonia, generating a NT-containing silica framework. This was then calcined at 300°C and converted into a polymerization catalyst. The PE composite made from this catalyst is shown in the right half of Figure 2. This catalyst achieved better uniformity than its magnesia analogue.

In summary, samples made by method C (polymerization) generally exhibited superior homogeneity to those prepared by B (coprecipitation). However, homogeneity was also largely dependent on the catalyst support used. Hisil 210 samples were the least homogeneous whereas the Syloid 244 and Cabosil EH-5 samples were more uniformly distributed. Method D (*in situ* gelation of the support around the NT) was also capable of producing highly uniform samples. Samples prepared by Method A (extruder blending) were superior in visual homogeneity to samples prepared by alternative methods, although other results indicate these samples were not homogeneous on a microscopic scale. It should likewise be noted that while samples generated from methods B–D exhibited varying degrees of uniformity, further blending by extrusion significantly improved their visual appearance. However, once again this visual improvement does not imply enhanced dispersion of the individual NT on a microscopic scale, as is indicated from other data below.

Electrical conductivity

Like graphite, SWNT exhibit extraordinarily high electrical conductivity. Therefore, this property can be another effective and direct measure of nanotube dispersion within PE/NT composites. Extruder blending has been shown to be relatively ineffective as a means of dispersing SWNT in PE because of the high affinity of NT for itself in comparison to the polymer. Figure 3 shows the results of some other mixing techniques. In series 3A the pure nanotubes (P-NT) were dispersed according to method B, i.e., they were suspended by sonication in a PE/TCB solution, which was then instantly “quenched” by

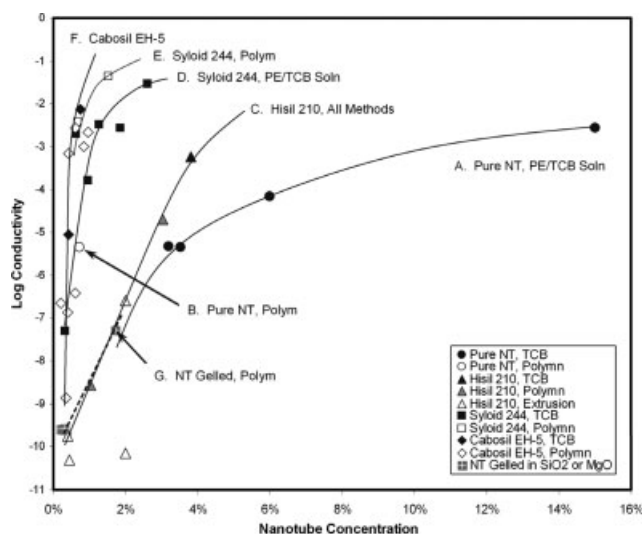


Figure 3 Conductivity of various NT/PE composites.

rapid addition to cold alcohol. The conductivity of these materials increased as the NT concentration was raised from 3 to 15% by weight of the composite. Although some high conductivity values were achieved at the highest loading, in reality this is not much better than is obtained from extrusion blending of NT or even of conductive carbon black. This suggests that the NT are not dispersed well by this preparation.

Dispersion by polymerization (Method C) was also attempted using pure NT. For the level of NT loading, much higher conductivity was obtained for point B than for series A in Figure 3. That is, polymerization (Method C) was much more effective at dispersing the NT than coprecipitation (Method B). Presumably catalyst particles were formed around and between the nanocomposites. Polymer was then generated, expanding and separating the nanotube agglomerates.

Interestingly, the conductivity from dispersion Method B was much improved when SS-NT was used as the source of the NT, i.e., when the unpurified NT, still attached to the silica catalyst, were used. Normally in P-NT preparation, the NT are separated by dissolving the silica catalyst away, which frees the NT and permits them to agglomerate into "ropes" or bundles that are then very difficult to disperse. By using the spent-catalyst as the source of NT, the original NT orientation is likely maintained. Apparently, this original orientation provides for a better dispersion in PE than the purified NT. Figure 3 line C shows the effect of dispersing SS-NT from the Hisil-210 silica catalyst by method B, i.e., into PE solution followed by quenching. The conductivity of this SS-NT sample (solid triangular point in line C of Fig. 3) is superior to the samples of analogous P-NT concentration (line A in Fig. 3).

For comparison, Figure 3 also shows the conductivity of Hisil 210 SS-NT when dispersed by intensive mixing extrusion (method A) at 160°C for 15 min (hollow triangular points in line C of Fig. 3). This method gave mixed results; some, but not all, of the composites have superior conductivity to composites made from purified NT in line A. The best of these extrusion mixed composites were equivalent to other composites made from Hisil 210 by method B.

Also shown in line C of Figure 3 is the conductivity of Hisil 210 SS-NT when dispersed by polymerization itself, Method C. After formation of NT the Hisil-210 catalyst was converted into a polymerization catalyst, and allowed to polymerize ethylene. The conductivity of these composites was very similar to the Hisil samples described above, which were dispersed in PE solution. This is to be expected since Hisil-210 is not polymerization grade silica, and a high degree of fragmentation is probably not achieved. Nevertheless, conductivity was still much higher than that observed from P-NT in 3A.

Figure 3, line D plots the conductivity of SS-NT using the Syloid 244 silica. Again the SS-NT was dispersed according to method B into PE/TCB solution which was then quenched in alcohol. The change in silica resulted in a major increase in conductivity. This is most likely due to the finer particle size of Syloid 244 (~ 5 μm) compared with Hisil-210 (100–200 μm). An additional boost in conductivity was obtained from the Syloid-244 when dispersion Method C was used, i.e., the polymerization method. This is shown in line E. This particular silica base is an excellent support for polymerization catalysts. It is the world's most commonly used industrial silica for ethylene and propylene polymerization because it disintegrates so effectively from internal polymer growth. Thus it is reasonable that, for this choice of silica, the polymerization method should give better conductivity than the PE/TCB solution method.

Still another silica support was tested and its conductivity is also plotted in Figure 3 as line F. Because of its pyrogenic origin, Cabosil EH-5 already has a submicron particle size. This version of SS-NT provided the most efficient NT utilization of those studied. Because of the ultra-fine particle size the two methods of dispersion B and C yielded similar results. Dispersion by polymerization was not greatly improved over dispersion in PE/TCB solution.

Composites made by dispersion Method D were also evaluated for conductivity and are shown in Figure 3, line G. NT was dispersed in aqueous or polar solution containing a magnesium or silicon compound which could be gelled around the NT. Then the NT/oxide complex was converted into a polymerization catalyst. Two of these composites contained magnesia as the oxide matrix, and the

TABLE I
Conductivity Before and After Intensive Mixing Extrusion

Treatment	Dispersion method	Base support	% NT in composite	Log conductivity
Before Extrusion	C, Polym	None	0.74%	-5.35
Extruded 5 min	C, Polym			-5.89
Extruded 15 min	C, Polym			-7.89
Before Extrusion	C, Polym	Hisil 210	1.03%	-8.57
Extruded 15 min	C, Polym			<-9.61
Before Extrusion	C, Polym	Hisil 210	3.03%	-4.70
Extruded 15 min	C, Polym			-9.23
Before Extrusion	C, Polym	Cabosil EH-5	0.22%	-6.65
Extruded 15 min	C, Polym			<-11.1

third, silica. All three samples have similar conductivity, in comparison to the NT loading. This method was not highly effective.

Summarizing these results, it would seem that dispersion by polymerization did offer an advantage in two cases over other methods. However, the choice of silica was very influential.

An attempt was made to see if high energy extrusion mixing could further improve the conductivity of composites made by polymerization. Four samples made by Method C were subjected to intensive extrusion mixing for 5–15 min at 240–260°C. Conductivity was measured before and after this treatment. One composite was sampled after one brief pass through the extruder, then the treatment was continued for the full duration. In all cases the conductivity decreased with extrusion, and the longer the extrusion, the lower the conductivity became. This data is presented in Table I. Evidently extrusion either breaks the NT or to some extent permits their re-agglomeration. Degradation of NT during processing has been reported by others as well.^{2,27}

Sometimes the conductivity of these composites, especially those having a low nanotube content, seem to be pressure sensitive, and for that reason a steel clamp was always used to take conductivity measurements. An attempt was made to quantify this relationship. Three composite plaques (5.1 cm × 5.1 cm × 1.25 mm) were placed in a hydraulic press between layers of polished brass. Wooden blocks were used to transmit force to the brass and thereby insulate the circuit from the press. The conductivity was then measured for these samples as a function of applied pressure. One result is shown in Figure 4.

In each test, conductivity improved by over an order of magnitude with increased pressure, eventually leveling off at some maximum value. The relationship was found to be reversible; after full pressure had been applied the force was reduced back to lower levels, which is shown by the solid colored point in the graph. As the pressure was released the same curve could be generated again in reverse. After full release of the pressure, the force

could then be re-applied resulting in the same curve again. This pressure dependence was found for most samples tested, including those made by dispersion methods B and C, although the effect was stronger in some cases than others.

The cause of this dependence on pressure is not entirely clear. Possibly, compression causes the NT to make better contact with each other within the composite. However, there was no observed deformation of the plaque; its thickness remained constant during the process. Intrinsic dependence of NT conductivity on pressure has been reported, although at much higher pressures.²⁸ Alternatively, pressure might improve contact at the surface with the metal plate electrode. For example the surface of the plaque, although glossy smooth, still has microscopic roughness and is possibly rich in polymer that tends to insulate the NT from contact with the metal lead. One could imagine that some applied pressure smoothes out ridges in the surface allowing the more rigid NT to penetrate up from underneath, making electrical contact with the metal plate.

To test this idea, metal foil, 2 cm × 2 cm, was imbedded on both sides of the plaque by compression molding at 180°C. Brass was used as a first attempt, but brass did not adhere well to the

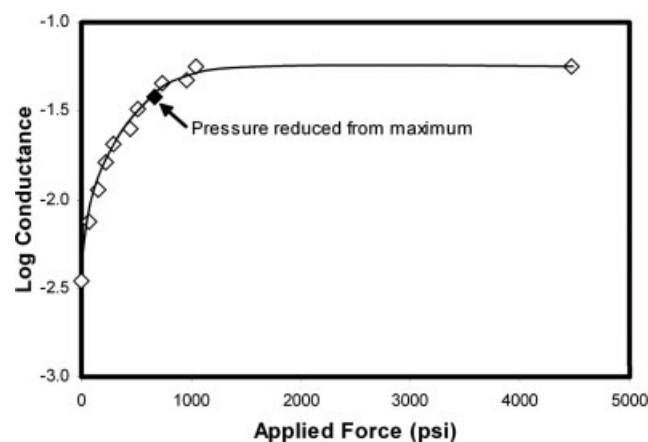


Figure 4 Conductivity dependence on applied pressure.

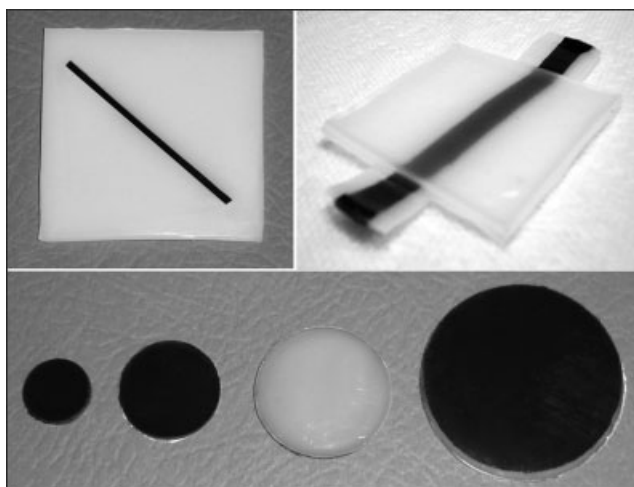


Figure 5 Molded articles with conductive strip or face.

composite. In a second test, heavy aluminum foil did adhere well. After the two pieces of metal had been pressed onto the molten plaque, they could not be easily removed. When the leads of the voltmeter were lightly touched to the two aluminum surfaces (no pressure applied) immediate conductivity was noted. In contrast, lightly touching the leads to this particular plaque itself generated little or no conductivity until some pressure was applied. The conductivity measured between these metal surfaces did not change with applied pressure, but it did match the conductivity measured in the normal way with applied pressure. Thus, it would seem that the pressure dependence is indeed a surface effect.

Many of these composites were quite conductive, and easily molded into films or filament. These films or filaments could then be press-molded onto other plaques or plastic parts to form a strip of black conducting polymer running on top of or through a normal white insulating polymer. In this way PE parts could be molded to contain internal conducting nonmetallic wires. Similarly one side of a sheet can be made conducting and the other insulating. Some examples are shown in Figure 5. This illustrates how the unrefined NT can be used in small amounts for many PE applications where conductivity is desired. Examples include drums and fuel tanks where it would be advantageous for some part of the tank, and not necessarily the whole container, to be conductive to prevent static. Multiple layered parts in blow molding, blown film, extruded pipe, and cast geomembrane are already quite commonly manufactured and a small amount of SS-NT composite could be added in a very thin external layer to afford conductivity.

Melt rheology

Melt rheology was obtained on all composites at 190°C using a parallel plate viscometer. The degree

of melt elasticity in PE is important because it determines much of the processing behavior of the molten polymers.^{29–32} It was immediately apparent that carbon NT, using all dispersal methods, exert a powerful influence on melt behavior. Even small amounts of NT greatly increased the viscosity at all shear rates, and especially at low shear rates, which results in a high degree of shear thinning. Certain PE grades from chromium or metallocene catalysts exhibit some shear-thinning character, while other PE grades like those from the Ziegler catalysts used here, display little.^{32,33} This suggests that the NT, with their unusually high aspect ratio and stiffness, can become entangled enough with polymer chains to inhibit motion. Because of this unusually strong response the normal Carreau-Yasuda equation could not be applied, for the most part, to these data. In many cases these viscosity curves, or their viscoelastic derivatives, showed evidence of two populations widely separated in their relaxation behavior. The two observed contributions represent the two components in the composite, i.e. polymer and NT. Such behavior is typical when inorganic filler is added to PE, but in the case of NT, the magnitude of the response was extreme.

Figure 6 shows the viscosity curves for several composites made by Method B using purified nanotubes (P-NT and PE coprecipitated from TCB solution). Only the nanotube concentration was varied. The same polymer base was used in all cases. Melt viscosity was found to increase with nanotube concentration at all shear rates, and especially at low shear rates where viscosity increased by several orders of magnitude. Carbon black added to PE produces a similar effect, but at a much higher filler concentration.

Figure 7 plots another series of viscosity curves of several composites made by preparation Method C (polymerization by SS-NT) using Hisil 210 silica as the base. Again one can see that viscosity increases

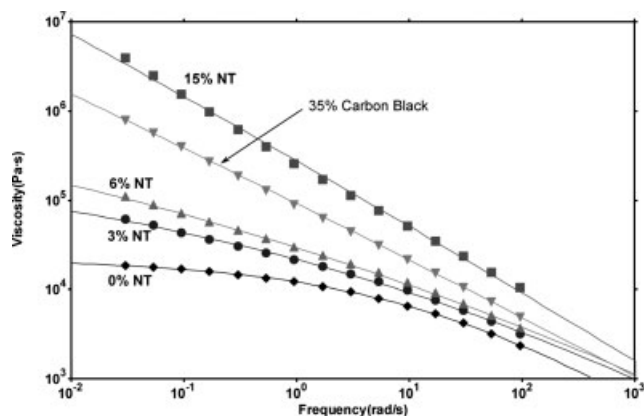


Figure 6 Effect of P-NT on dynamic viscosity at 190°C when dispersed by method B.

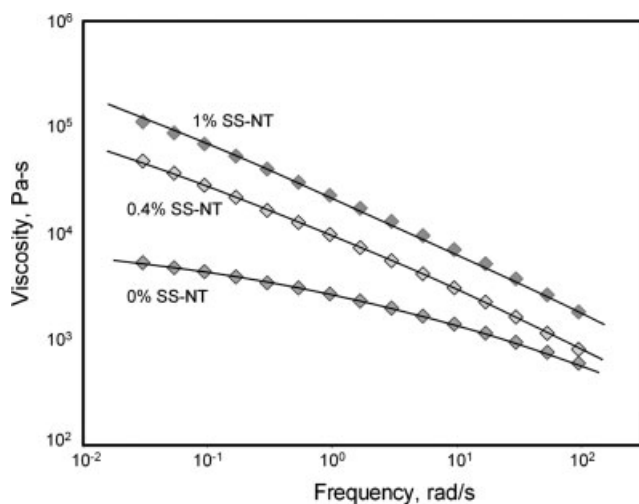


Figure 7 Effect of SS-NT on dynamic viscosity at 190°C. PE made by polymerization from Hisil 210; viscosity corrected for silica.

with NT concentration. However, by comparing Figures 6 and 7 it is clear that for a given NT concentration, the effect is much greater in Figure 7. This is due to the replacement of P-NT by SS-NT, especially with dispersion method C. Much less NT is required in Figure 7 than in Figure 6 to achieve similar enhancements in viscosity.

When comparing the viscosity of P-NT composites in Figure 6 to those made from SS-NT in Figure 7 it is necessary to take into account the effect of the silica support. SS-NT may typically contain several times more silica than NT, depending on the degree to which NT production is allowed to take place on the silica. The viscosity contribution from silica is not very high in the 0–10% filler range; nevertheless control runs were made containing 0–25% silica without NT. Rheology curves were then obtained from these control samples and this calibration series was then used to subtract the contribution of the silica. Thus in Figure 7 the contribution from silica has been mathematically removed, leaving only the contributions from the PE and NT.

Even after correction for residual silica it is clear that SS-NT is a powerful promoter of low-shear viscosity. It is interesting to compare the viscosity enhancement from NT with that from other fillers. Similar PE resins were blended with amorphous carbon black, perhaps the closest conventional filler to NT by chemical composition. Having a particle size of several microns, carbon black is widely used as an additive in commercial PE to provide ultraviolet light protection. The normal loading of 2% has a negligible effect on melt viscosity, but the masterbatch blend can sometimes contain as much as 35 wt % carbon black. At this level there is a noticeable increase in viscosity. An example is shown for

comparison in Figure 6. However, the magnitude of this increase from 35% carbon black is equivalent to a considerably lower level of NT from SS-NT or even P-NT, as shown in Figure 6.

Melt viscosity is also dependent on the molecular weight of the polymer produced.^{21–23} In fact the low shear viscosity is expected to vary linearly with M_w when plotted on a log–log graph. Such a plot is shown in Figure 8, in which the viscosities at 0.01/sec of the composites are shown. A number of “control” polymers were made from similar catalysts, containing no NT. The molecular weight was varied over a wide range to establish a reference line. These constitute the first group of polymers shown in Figure 8 (gray squares), and one can easily see the linear relationship between $\log \eta_{(0.01)}$ and $\log M_w$. This line is similar to the so-called “3.4 power law” or “Arnett” line obtained for linear PE,^{23,32} except the measured low-shear viscosity is used instead of the extrapolated zero-shear viscosity. This modification was convenient within this limited data set because it was not possible to extrapolate the extreme viscosity behavior observed from the composites containing NT. Notably, the 0.01/sec viscosities of the nanotube-containing composites do not fall on the control reference line. Several data series are shown, representing different ways of dispersing the NT. The contribution from silica has been subtracted from these data. In each series the low-shear viscosity rises further above the PE reference line as the NT concentration is raised.

In Figure 9 the amount of deviation from the line is plotted as a function of the nanotube concentration in each polymer. That is, $\log(\eta/\eta_{ref})$ is plotted against wt % NT. The different methods of dispersion become distinct under this comparison. Again P-NT dispersed by Method B (PE/TCB solution) resulted in the least effective use of NT. In contrast,

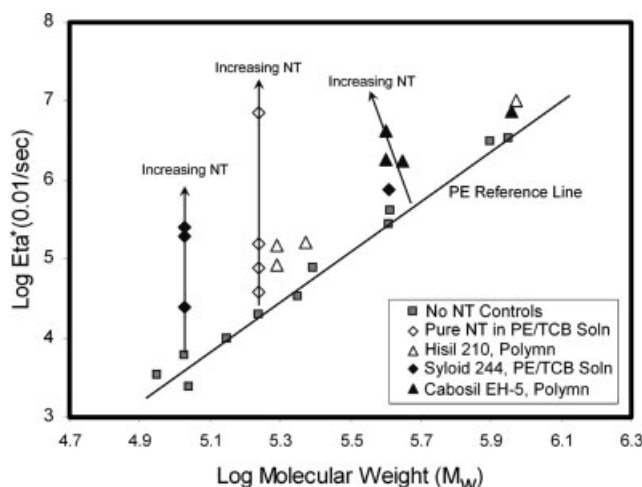


Figure 8 Power law plot showing effect of NT on dynamic melting viscosity.

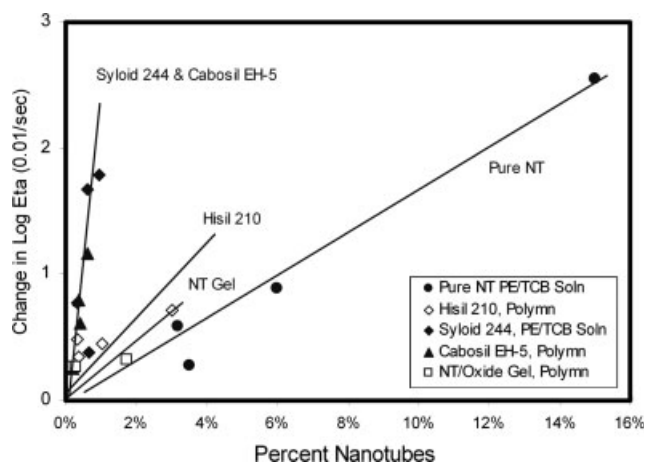


Figure 9 Effect of NT on dynamic viscosity at 0.01/s.

using the fine silicas and either dispersion Method B or C, NT were used most effectively. The former method required roughly 12 times more NT than the latter to achieve the same change in viscosity. The data did not allow further distinction between polymerization and PE/TCB solution. Hisil 210 SS-NT exhibited varying performance, as did composites made by method D (cogelling NT with catalyst).

An attempt was made to understand whether extrusion mixing could further enhance the dispersion of SS-NT composites, and thus increase their effectiveness. Two composites were placed in a laboratory twin-screw mixing extruder in which the molten polymer could be recirculated continuously for about 15 min. Rheology was obtained from these samples before and after extrusion at 240–260°C. About 0.2% BHT was added for stabilization. The melt viscosity curves from these experiments can be seen in Figure 10. In neither case was extrusion found to further enhance the viscosity. Instead, extrusion actually lowered the viscosity at all shear rates. This decrease in viscosity might be due in part to mechanical degradation of the polymer, even in the presence of BHT. Another possibility, consistent with the results from electrical measurements, is that the NT agglomerate or perhaps break during intensive extrusion, becoming less effective.

Finally, a VanGurp-Palmen plot of these composites is shown in Figure 11. This type of plot is often used to judge the elasticity of PE samples.^{34,35} In general, linear PE shows a smooth curve progressing to 90° at low frequencies. Other shapes, not moving toward 90° on the left, indicate high elasticity, which can come from many sources. Some of the shapes can be considered extreme. Many of the composites turn down, then back up, which indicates contributions from two components exhibiting vastly different relaxation behavior. Clearly these contributions are in this case attributable to the polymer and the NT that make up these composites.

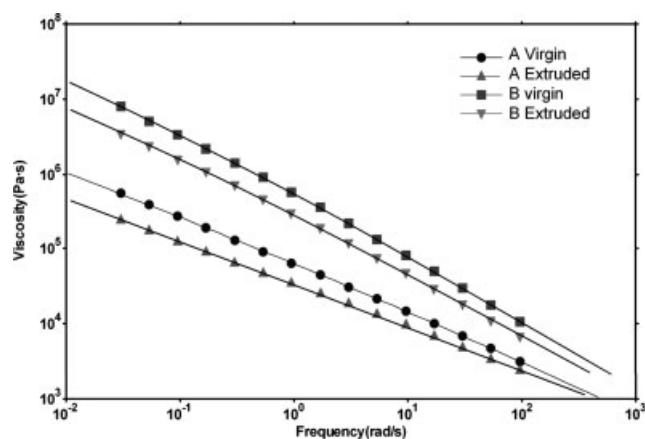


Figure 10 Effect of extrusion mixing on NT composites. A: Hisil 210 SS-NT 1% NT, (B) Cabosil EH-5 SS-NT 0.25% NT.

The samples in Figure 11 were all made from unsupported NT, i.e., P-NT. Using dispersion Method B the relaxation behavior become more “bimodal” as the nanotube concentration increased. However, in one of the samples in Figure 11, the P-NT was dispersed by polymerization, and although this sample’s P-NT concentration was the smallest of any represented, this sample nevertheless displayed the most unusual behavior. Composites made from SS-NT instead of P-NT displayed similar “bimodal” relaxation behavior, although at lower NT concentrations that in Figure 11.

Physical properties

To determine the effect of NT on the physical properties of PE, flexural modulus and tensile modulus were determined from various composites. Despite the high aspect ratio, NT incorporated by these methods had much the same effect on physical properties as other fillers. Flexural modulus was

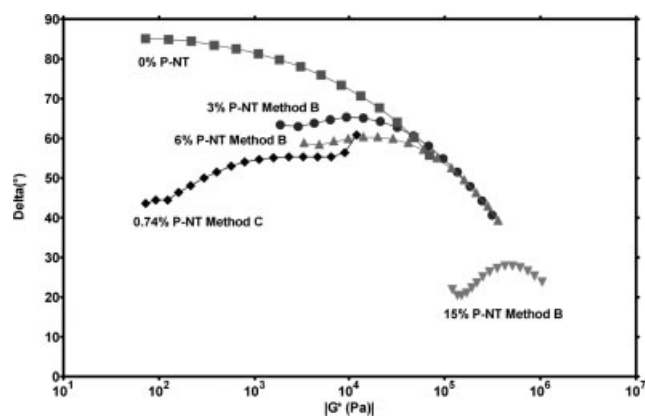


Figure 11 Delta versus complex modulus at 190°C for composites made from P-NT either by method B (suspension in PE/TCB solution) or by C (polymerization).

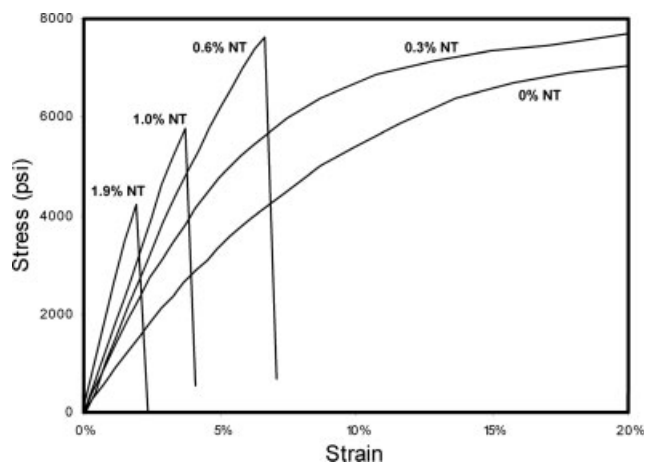


Figure 12 Flexural curves for composites made by method B using SS-NT on Syloid 244 silica.

increased by the NT, but at the expense of flexibility and toughness. Figure 12 shows the stress–strain curves for the composites made from Syloid 244 SS-NT by preparation B, i.e., suspended by sonication in PE/TCB solution, followed by quenching. The initial slope of the lines (the modulus) increases with increasing nanotube concentration. However, the stiffer samples also become brittle and tend to break more quickly. This behavior is typical of many fillers in PE, and it probably indicates a lack of adhesion between filler and matrix.^{2,27,36} P-NT based composites were also tested with similar results, although requiring higher NT concentrations per effect. Because of the presence of silica in the SS-NT composites it became very difficult to distinguish the effects of the NT from that of silica.

In general, tensile tests on these composites yielded much the same behavior as the flexural tests. NT increased the modulus but at the expense of elongation. Figure 13 shows a typical tensile stress–strain curve for one series. The composites in this group were all from preparation B, precipitation of refined NT from PE/TCB solution. The strain is plotted on a log scale so that one can fully see how the NT increase the initial slope (the modulus) but decrease the degree of elongation. Notably, there is a large loss in elongation between 3 and 6% NT in this series.

Composites made from SS-NT instead of P-NT likewise exhibited similar tensile behavior, except at lower NT concentrations. Once again it is difficult to distinguish the effect of NT from that of the silica carrier. To address this problem a series of control composites were made containing 5–25% Syloid 244 silica, but no NT in any form. The modulus from this series is plotted in Figure 14 as a function of the amount of silica added. This series is the reference line. Other composite series, containing both NT and silica, are also plotted for comparison. The nanotube content

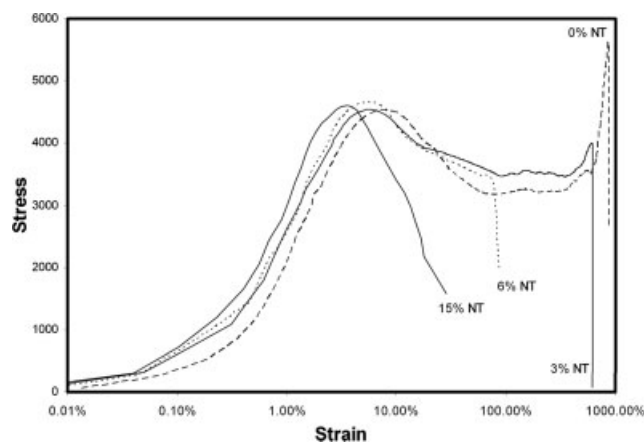


Figure 13 Tensile curves for composites made by method B using P-NT.

in some of the better samples is labeled nearby. Although there is scatter in the data, this method provides a rough estimate of each method's effectiveness.

Composites made from P-NT by Method B can be seen along the Y-axis. There is no doubt that NT increase the tensile modulus, and the effect increases with NT content. Several SS-NT composites made by Methods B and C also stand well above the reference line, indicating a strong effect from NT. In those cases it takes a much lower NT content to similarly increase the modulus, indicating a greater effectiveness of SS-NT compared to P-NT.

CONCLUSIONS

These nanotube-PE composites have been investigated by rheological, flexural, tensile, and electrical tests, each yielding similar conclusions. In PE, refined NT (P-NT) are much less effective as a filler

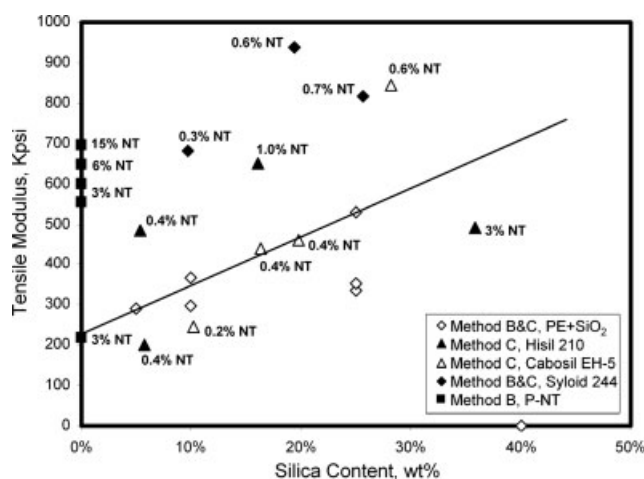


Figure 14 Tensile modulus for composites made by methods B and C.

than SS-NT. Furthermore, results among the SS-NT composites indicate that the choice of silica can also have a major influence on the final properties. The following order of effectiveness was consistently observed: Cabosil EH-5 > Syloid 244 » Hisil 210. Within a given family of composites using the same silica, results suggest that polymerization is the preferred method of dispersion.

All attempts to further homogenize the composite by intensive extrusion resulted in improved visual uniformity, but a loss of rheological and electrical properties. This again suggests that visual uniformity and "micro-dispersion" are not the same. Extrusion may even break NT or allow their agglomeration.

High conductivity was obtained in PE from low levels of NT. Conductivity could sometimes be detected even down to 0.25% NT. SS-NT based composites yielded far better results than P-NT. This suggests that refining the NT allows their agglomeration, which is very difficult to reverse. Converting the original SS-NT catalyst into a polymerization catalyst provides an efficient and low-cost method of dispersing the NT. The measured conductivity was also found to be pressure sensitive, probably from microscopic surface roughness, despite the glossy macroscopic appearance.

NT greatly increased the low-shear melt viscosity of PE. The effect of inert fillers like silica and carbon black on the melt rheology is well-known and is not comparable to that observed in this study from NT.

The refinement of NT constitutes a large proportion of the current manufacturing cost, because the silica catalyst must be dissolved away from the NT by HF or caustic solutions. This process also generates significant chemical waste. That SS-NT performed better in these tests than P-NT is an unexpected and promising find for future commercial applications.

The authors thank D.C. Rohlffing of Chevron-Phillips Chemical Co. and Professor Brian Grady of the University of Oklahoma for assistance with polymer characterization, as well as Southwest Nanotechnologies for use of materials and equipment.

References

- Benham, E. A.; McDaniel, M. P. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th ed.; Seidel, A., Ed.; John Wiley & Sons, Inc: Hoboken, 2006; Vol. 20, p 149.
- Andrews, R.; Weisenberger, M. C. *Curr Opin Solid State Mater Sci* 2004, 8, 31.
- Breuer, O.; Sundararaj, U. *Polym Compos* 2004, 25, 630.
- Colbert, D. T. *Plast Addit Compound*, 2003, 5, 18.
- Baughman, R. H.; Zakhidov, A. A.; deHeer, W. A. *Science* 2002, 297, 787.
- Kitiyanan, B.; Alvarez, W. E.; Harwell, J. H.; Resasco, D. E. *Chem Phys Lett* 2000, 317, 479.
- McDaniel, M. P. *Adv Catal* 1985, 33, 47.
- Niegisch, W. D.; Crisafulli, S. T.; Nagel, T. S.; Wagner, B. E. *Macromolecules* 1992, 25, 3910.
- Bonduel, D.; Bredeau, S.; Alexandre, M.; Monteverde, F.; Dubois, P. *J Mater Chem* 2007, 17, 2359.
- Peeterbroeck, S.; Lepoittevin, B.; Pollet, E.; Benali, S.; Broekart, C.; Alexandre, M.; Bonduel, D.; Viville, P.; Lazzaroni, R.; Dubois, P. *Polym Eng Sci* 2006, 46, 1022.
- Bonduel, D.; Mainil, M.; Alexandre, M.; Monteverde, F.; DuBois, P. *Chem Commun* 2005, 6, 781.
- Tong, X.; Liu, C.; Cheng, H.; Zhao, H.; Yang, F.; Zhang, X. *J Appl Polym Sci* 2004, 92, 3697.
- Giulio Lolli, G.; Zhang, L.; Balzano, L.; Sakulchaicharoen, N.; Tan, Y.; Resasco, D. E. *J Phys Chem B* 2006, 110, 2108.
- Resasco, D. E.; Herrera, J. E.; Balzano, L. *J Nanosci Nanotechnol* 2004, 4, 398.
- Resasco, D. E.; Alvarez, W. E.; Pompeo, F.; Balzano, L.; Herrera, J. E.; Kitiyanan, B.; Borgna, A. *J Nanoparticle Res* 2002, 4, 131.
- Kitiyanan, B.; Alvarez, W. E.; Harwell, J. H.; Resasco, D. E. *Chem Phys Lett* 2000, 317, 497.
- Jorio, A.; Santos, A. P.; Ribeiro, H. B.; Fantini, C.; Souza, M.; Vieira, J. P. M.; Furtado, C. A.; Jiang, J.; Saito, R.; Balzano, L.; Resasco, D. E.; Pimenta, M. A. *Phys Rev B* 2005, 72, 75207.
- Bachilo, S. M.; Balzano, L.; Herrera, J. E.; Pompeo, F.; Resasco, D. E.; Weisman, R. B. *J Am Chem Soc* 2003, 125, 11186.
- Herrera, J. E.; Resasco, D. E. *Chem Phys Lett* 2003, 376, 302.
- Hsieh, H. L.; McDaniel, M. P.; Martin, J. L.; Smith, P. D.; Fahey, D. R. *Macromolecular Symposium, Chicago; Advance in Polyolefins: The World's Most Widely Used Polymers*; Seymour, R. B., Cheng, T. C. Eds.; September 1985. Plenum Press: New York, NY, 1987; p 153.
- Janzen, J.; Colby, R. H. *J Mol Struct* 1999, 485/486, 569.
- Fetters, J.; Lohse, D. J.; Colby, R. H. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; AIP Press: New York, 1996; p 335.
- Arnett, R. L.; Thomas, C. P. *J Phys Chem* 1980, 84, 649.
- Bird, R. B.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids, Volume 1: Fluid Mechanics*, 2nd ed.; Wiley: New York, 1987.
- Hieber, C. A.; Chiang, H. H. *Rheol. Acta* 1989, 28, 321.
- Hieber, C. A.; Chiang, H. H. *Polym Eng Sci* 1992, 32, 931.
- Fisher, F. T.; Bradshaw, R. D.; Brinson, L. C. *Compos Sci Technol* 2003, 63, 1689.
- Chen, F.; Stokes, K. L.; Wang, H.; Fang, J.; Zhou, W. *Nanotechnology* 2003, 1, 144.
- Hogan, J. P.; Levett, C. T.; Werkman, R. T. *SPE J* 1967, 23, 87.
- Hogan, J. P. *J Polym Sci Part A-1: Polym Chem* 1970, 8, 2637.
- Hogan, J. P. In *Applied Industrial Catalysis*; Leach, B. E., Ed.; Academic, New York, NY, 1983; Vol. 1, Chapter 6, p 149.
- McDaniel, M. P.; Rohlffing, D. C.; Benham, E. A. *Polym React Eng* 2003, 11, 105.
- Jensen, M. D.; McDaniel, M. P.; Martin, J. L.; Benham, E. A.; Hawley, G. R.; Thorn, M. G.; Yang, Q.; Jayaratne, K.; Eaton, A.; McDaniel, N. D.; Sukhadia, A. M.; Rohlffing, D. C.; Shveima, J. S.; Lanier, T.; Deslauriers, P. J.; Wharry, S. In *MOSPOL 2004 Conference on Metallocenes*, Moscow, Russia, June, 2004.
- Trinkle, S.; Friedrich, C. *Rheol Acta* 2001, 40, 322.
- Trinkle, S.; Walter, P.; Friedrich, C. *Rheol Acta* 2002, 41, 103.
- Thostenson, E. T.; Chou, T. W. *J Phys D: Appl Phys* 2003, 36, 573.