# CARBON NANOTUBES: A HIGH PERFORMANCE CONDUCTIVE ADDITIVE

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INTRODUCTION

Multiwall carbon nanotubes were first synthesized in 1983 by scientists at Hyperion Catalysis International. These nanotubes are about 10 nanometers in diameter and 10 or more microns long. They are made by a continuous, catalyzed gas phase reaction of low molecular weight hydrocarbons. Current production capacity using this process is in the multiple tens of tons, with the capability to readily expand to meet demand. Figure 1 (Appendix) is a drawing of the graphitic multiwall structure, Figure 2 (Appendix) is a transmission electron microscope image of a portion of a nanotube showing the multiwall structure surrounding the hollow core, Figure 3 (Appendix) shows the curvilinear structure of multiwall nanotubes. Figure 4 shows the relative size of nanotubes compared to carbon fiber or carbon black.

Figure 4: Comparison of nanotubes with carbon fiber and carbon black
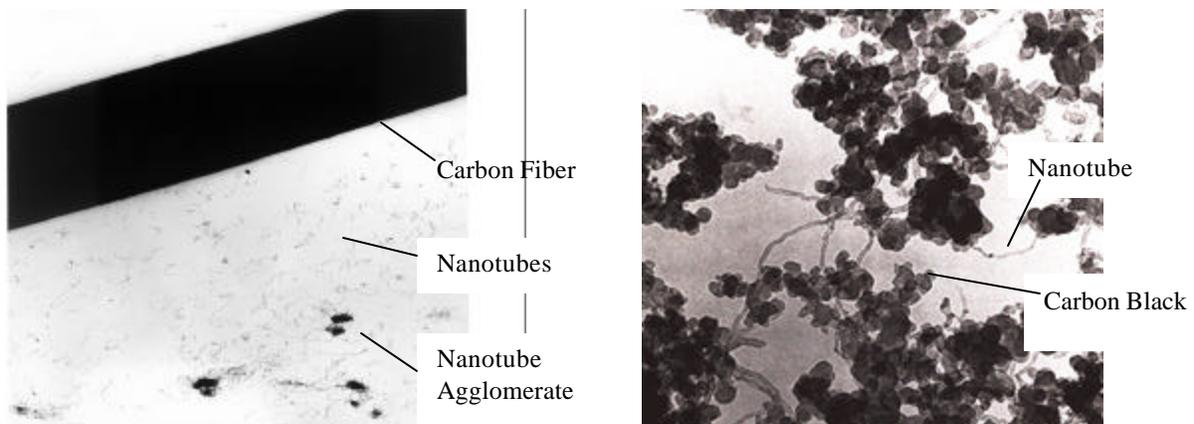
Carbon nanotubes have proven to be an excellent additive to impart electrical conductivity in plastics. Their high aspect ratio (1000:1) imparts electrical conductivity at lower loadings compared to carbon black, chopped carbon fiber, or stainless steel fiber, see Figure 5. The benefits of lower loadings of conductive additives, on both polymer properties and polymer viscosity, will be discussed in the balance of this paper.

Figure 5. Calculated Loading for Percolation as a Function of Aspect Ratio
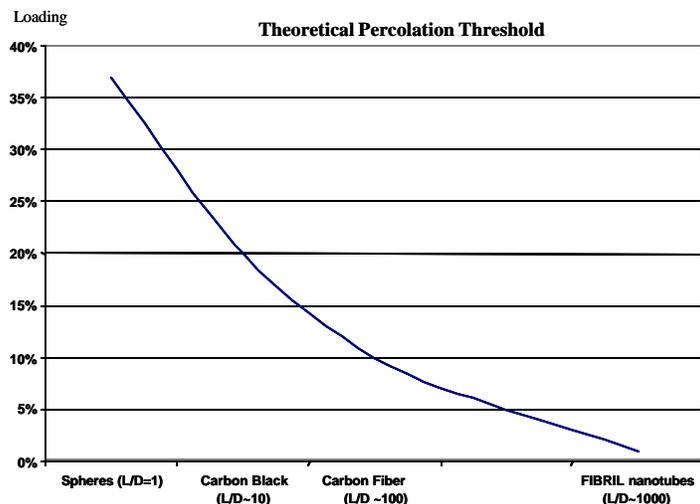
COMPARISON OF NANOTUBES WITH OTHER CONDUCTIVE ADDITIVES

A study has recently been completed evaluating three commercially available PC/ABS conductive compounds made with nanotubes, carbon fiber and carbon black. These three compounds were developed to offer approximately the same relatively low level of surface resistivity (i.e. high conductivity). Because of the different aspect ratios of the three additives, the level of additive required to obtain similar resistivities is different, see Table 1.

Table 1. Resistivity vs. Additive/Loading in PC/ABS

Additive	Loading wt. %	Volume Resistivity (ohm-cm)	Surface Resistivity (ohms)
None		10^E16	n.a
Nanotubes	7.3	$10^E1 - 10^E3$	$10^E4 - 10^E6$
Carbon black	16.7	$<10^E3$	$<10^E6$
Carbon fiber	13.7	$<10^E3$	$<10^E6$

NANOTUBES MAINTAIN MORE OF THE RESIN'S DUCTILITY

As seen in Table 2., nanotubes preserve more of the neat resin's elongation at break and unnotched Izod compared to carbon black or carbon fiber. The addition of any particulate additive to engineering resins results in a decrease in resin ductility. This can be dangerous in applications where loss of resin toughness can hurt the performance of a part. The small size and low loading of nanotubes minimizes the adverse effect on the ductility of the resin. It should be pointed out that the loading of nanotubes used in this study is higher than normal for ESD applications. We will show later in this paper that 2 to 3% nanotubes in polycarbonate are sufficient for ESD levels of conductivity. In addition, it has been found that measuring volume resistivity is more accurate than measuring surface resistivity as a predictor of a material's ability to bleed off static charge. The net effect is that at lower loadings needed for real world ESD performance, a 2-3% loading of nanotubes would give an even greater maintenance of the neat resin properties.

Table 2. Effect of Additive/Loading on Ductility

Additive	Loading (wt. %)	Elongation At Break (%)	Unnotched Izod (ft lbs)
None		100	NB
Nanotubes	7.3	10+	30
Carbon black	16.7	3	10
Carbon fiber	13.7	1 - 3	4

NANOTUBES GIVE THE SMOOTHEST PART SURFACE

Because of their small size and low loading, nanotubes have less of an effect on part surface quality. The addition of most particulate additives to thermoplastics results in a decrease in the surface quality of the

part which is detrimental when making appearance parts for automotive or for many electronic applications, as will be explained later. A numerical measure of surface smoothness was made using a Mahr Federal Perthometer on plaques molded in a mirror surface tool. Table 3 shows the arithmetic average of the surface roughness.

Table 3. Average Surface Roughness (Ra) vs. Additive/Loading

Additive	Loading (wt. %)	Ra (μ m)
None		0.019
Nanotubes	7.3	0.025
Carbon black	16.7	0.035
Carbon fiber	13.7	0.426

NANOTUBES GIVE LOW PART WARPAGE

Nanotubes are very much smaller than other additives, thus are more insensitive to shear. The result is they form isotropic (random) distributions within molded parts. Large additives are frequently affected by the levels of shear commonly found in injection molding. This can give uneven distribution of the additive within a part, especially one that has corners, openings or other three dimensional details. For conductive additives this means uneven levels of conductivity at different spots on a molded part.

Figure 6 (Appendix) shows a light transmission photomicrograph of a microtomed section of the carbon fiber filled injection molded tensile bar. At 230x magnification it is easy to see the alignment of the carbon fibers in a section of the part. Figure 7 (Appendix) shows a Transmission Electron Microscope (TEM) view of an ultramicrotomed section of the nanotube-filled tensile bar. It can be seen that the nanotubes are randomly aligned. This insures a uniform level of conductivity throughout the most complex part or for large parts with multiple gates.

Another advantage of the isotropic distribution of nanotubes is a reduced chance of part warpage. Table 4 shows the difference in shrinkage in the flow direction vs. shrinkage in the transverse direction for the three compounds.

Table 4. Effect of Additive/Loading on Differential Shrinkage

| Additive	Loading (wt. %)	Differential Shrinkage (a)
None		1.03
Nanotubes	7.3	0.96
Carbon black	16.7	0.97
Carbon fiber	13.7	0.92

(a) Ratio of shrinkage in flow direction divided by
   shrinkage in transverse direction.

It can be seen that the differential shrinkage for the very high aspect ratio nanotube-filled compound is almost the same as the nearly spherical carbon black and much less than for carbon fiber. This means that part warpage will likely be much lower with nanotubes than carbon fiber.

NANOTUBES GIVE THE LEAST EFFECT ON RESIN VISCOSITY
Another advantage of the low loading of nantoubes is that they do not raise the viscosity of the compound as much as the higher loading of larger fillers, see Fig 8. This means that thin walled or large multi-gated parts may be more easily filled.

Fig. 8. Effect of Additive Loading on Resin Viscosity
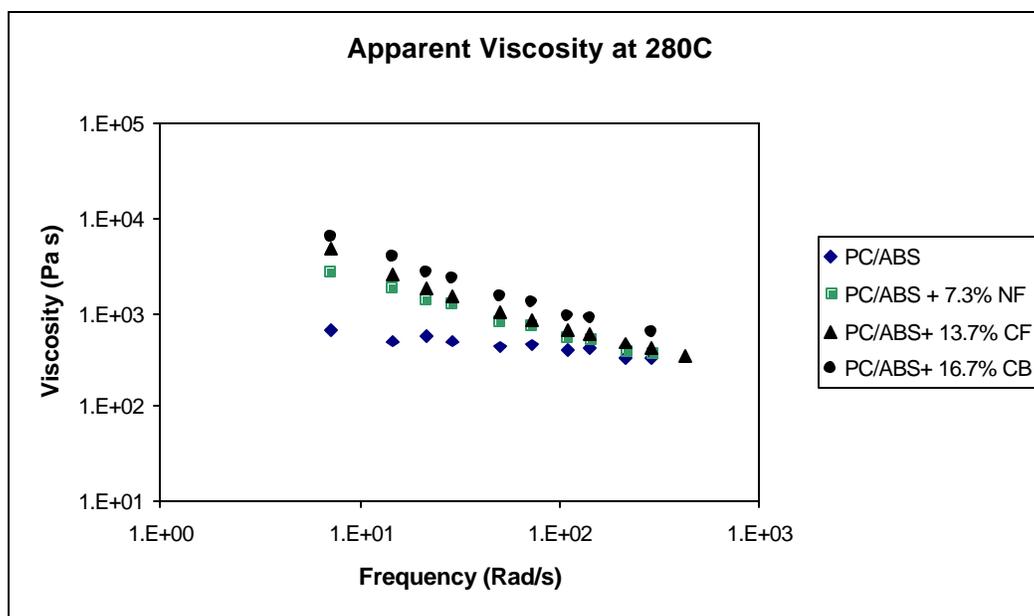
RECOMMENDATIONS FOR LETTING DOWN NANOTUBE MASTERBATCHES
As stated in the introduction, the as-made nanotubes intertwine into agglomerates (see Figure 4). As shown by the isotropic distribution of the nanotubes in molded parts, the small size of the individual nanotubes makes them insensitive to shear fields. Thus, the as-made nanotubes are difficult to disperse. In order to insure consistent, high quality dispersions, Hyperion performs the initial dispersion of the nanotubes by making masterbatches of 15 to 20% concentration by weight. It is important that the letdown process be done thoroughly, a poor letdown gives a non-homogeneous mixture of the high viscosity masterbatch resin with the lower viscosity let-down resin. This two-phase mixture will perform as if the nanotubes were poorly dispersed, when, in fact, the dispersion is good, but the mixing is the issue.

Recently a study was completed that can guide a compounder who wants to let down Hyperion's masterbatches into high quality compounds. Starting with Hyperion's 15% polycarbonate masterbatch, a twin screw extruder was used to make let-down compounds containing nanotubes at 0.5%, 1%, 2% and 5% by weight. The dynamic rheological performance of the various compounds as well as the volume resistivity was then analyzed. See the Experimental section for complete details on the procedure and equipment.

The complex viscosities of the nanotube masterbatch, the pure polycarbonate (PC) and the diluted composites are shown in Fig. 9.

Fig. 9. Viscosity of Masterbatch, PC and Let-down Compounds at Different Rheometer Frequencies (Shear Rates).
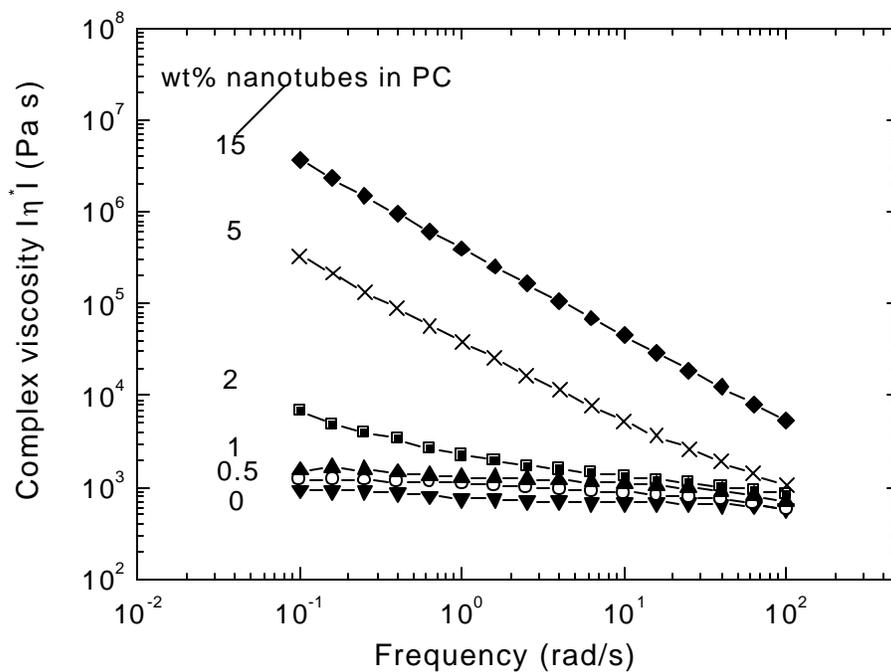
The masterbatch is orders of magnitude more viscous than the pure PC even at high shear rates and exhibits a very strong shear thinning effect. In contrast, the PC shows only a small shear dependence. The complex viscosity of the different let-downs increases with the nanotube content. The effect of the nanotubes is most pronounced at low shear and the relative effect diminishes with increasing shear due to shear thinning. It is interesting to note that the viscosity curves for 0.5% and 1 % nanotubes have similar shear dependencies as the pure PC, revealing a Newtonian plateau at low shear. However, above 2% nanotubes, the rate at which the complex viscosity decreases with shear is nearly identical to that of the 15% masterbatch, that is the viscosity curve is nearly linear over all the range of shears shown.

The volume resistivity of the various let-down compounds were measured to give an accurate percolation curve for nanotubes in polycarbonate, Fig.10. It can be seen that the percolation threshold is between 1% and 2% in these well-mixed samples. At 2% loading, the conductivity is well within the range needed for most electrostatic dissipative (ESD) applications. Thus, the advantages in physical properties that were demonstrated previously with 7.3% nanotubes in PC/ABS will be expected to be even greater at this lower loading. Of course the percolation point will be expected to be different in different polymers, as morphological differences such as the
degree of crystallinity and the presence of multiple polymer phases, can have an effect on the amount of filler needed to reach the percolation point.

Fig. 10. Percolation Curve for Nanotubes in Polycarbonate
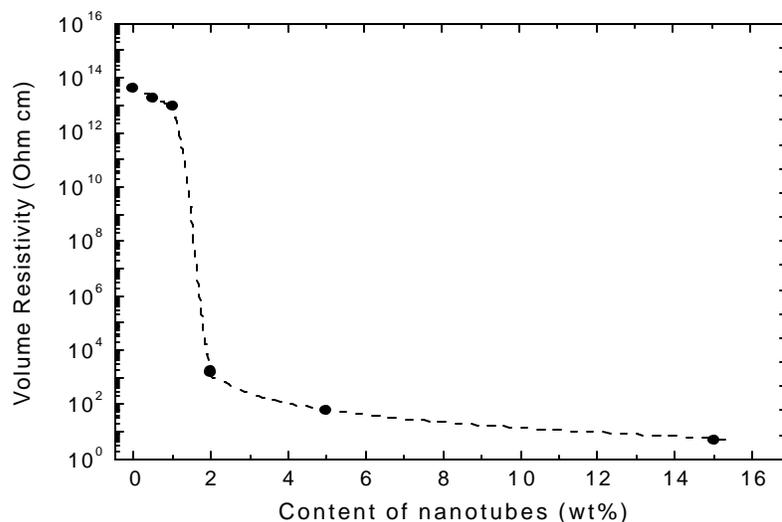
APPLICATIONS
Carbon nanotube-filled plastics are being used in several commercial automotive applications in North America, Europe and Japan. One application area is in fuel lines. Nylon 12 is frequently the resin of choice for these fuel lines because of its chemical resistance to gasoline. Because moving fuel can build up a static charge, the fuel line needs to be conductive enough to bleed off the charge. Nanotubes are the preferred conductive additive for this application due to the low loading necessary. This preserves more of the tensile elongation of the resin. This reduces the chance of a fuel line rupture in a low temperature accident. Other advantages of the low loading of the very small nanotubes is that they do not dilute the barrier properties of the resin to the permeation of gasoline vapor. This is important in insuring that the vehicle does not exceed the allowed total hydrocarbon losses allowed under the Clean Air Act. As the Clean Air Act reduces the allowable losses of hydrocarbons, the fuel lines have moved to a multi-wall construction using a resin with a high barrier than nylon 12. Here the carbon nanotubes are mixed with the innermost layer and because of their small size and low loading, allow the extrusion of thin, ductile inner walls as part of the co-extruded structure.

Another application area that has found success in Europe is thermoplastic fenders for in-line electrostatic painting in conjunction with steel panels. In order to survive the E-coat bake oven temperatures, high heat polymers must be used. Electrostatic spray painting must be used in order to apply the topcoats with minimal wasteful overspray, minimal emissions of solvents and with high quality appearance. This means the thermoplastic fenders need to be conductive. Having a conductive plastic is much preferred to spraying a conductive primer on before the topcoats. The low loading and small size of carbon nanotubes allow an as-molded Class A surface. In addition, the low loading preserves more of the resin's ductility so that the fender will not exhibit an undesirable brittle failure that could spray sharp shards through the air, in a low temperature impact. As end-of-life recycling laws take effect we expect more car manufacturers to switch to thermoplastic fenders and doors utilizing nanotubes.

Nanotube-filled polycarbonate (PC), polyetherimide (PEI) and polyetheretherketone (PEEK) are also used in the electronic industry for their ability to provide a very smooth, hard, surface to minimize "sloughing" or "rub off" of particles from the surface of a molded part. In the manufacture of semiconductor chips, the least static discharge can obliterate the small features that are so painstakingly photolithographically etched on the surface. So the wafers are transported from station to station in FOUPS (Front Unloading Unified Pods) that have conductive plastic in all wafer contact points. But it is not enough for the plastic to be just ESD conductive, the part surface should be very hard and smooth to prevent sloughing of particles as the wafers are inserted and removed in the FOUP. In the hyperclean environment needed for chip manufacture, one free particle can destroy hundreds of thousands of dollars of product.

Similar concerns about static control and sloughing have led to the widespread use of nanotube filled polycarbonate in transport trays, as well as actual components, for the manufacture of computer hard disc drives.

EXPERIMENTAL PROCEDURE FOR RHEOLOGY STUDIES

A Haake co-rotating, intermeshing twin-screw extruder (length D=30mm, L/D=10, barrel temperature of 240°C, screw speed of 280 rpm and a feed rate of 980 gram/hour) was used to make letdowns from the Hyperion polycarbonate masterbatch. The screw configuration contains two kneading disc blocks located at 35 and 147 mm, respectively, from the hopper. Both kneading disc blocks consist of one right-handed medium-pitched (L/D = 1.0), one left-handed medium-pitched (L/D = 1.0) kneading disc elements and one mixing ring. The letdown polycarbonate was Mitsubishi Engineering Plastics E-2000, a high viscosity extrusion grade with a published melt viscosity of 5.3g/10minutes (at 300°C, 1.2 Kg weight by method ISO1133).

Polycarbonate compounds were compression molded into samples that were evaluated by dynamic rheology on an ARES (Advanced Rheometric Expansion System) rheometer from Rheometrics, Inc. The measurements were carried out in an oscillatory shear mode using parallel plate geometry at 260C under nitrogen. Frequency sweeps between 0.1 and 100 rad/s were carried out at low strains (0.1 – 10%) and were shown to be within the linear elastic range for these materials. The upper limits of the viscoelastic range, determined in strain sweeps at 10 rad/s, were found to decrease with nanotube content. Repeated sweeps with increasing and decreasing frequencies showed that the material is stable

under the measurement conditions. Specimens were placed between the preheated plates and were allowed to equilibrate for approximately ten minutes prior to each frequency sweep run. The obtained values were corrected to the true volume between the plates. All polycarbonate samples were dried for a minimum of 16 hours at 80°C in a vacuum oven prior to processing or rheological measurements.

ACKNOWLEDGMENTS

APPENDIX

Figure 1. Structure of Multiwall Carbon Nanotubes
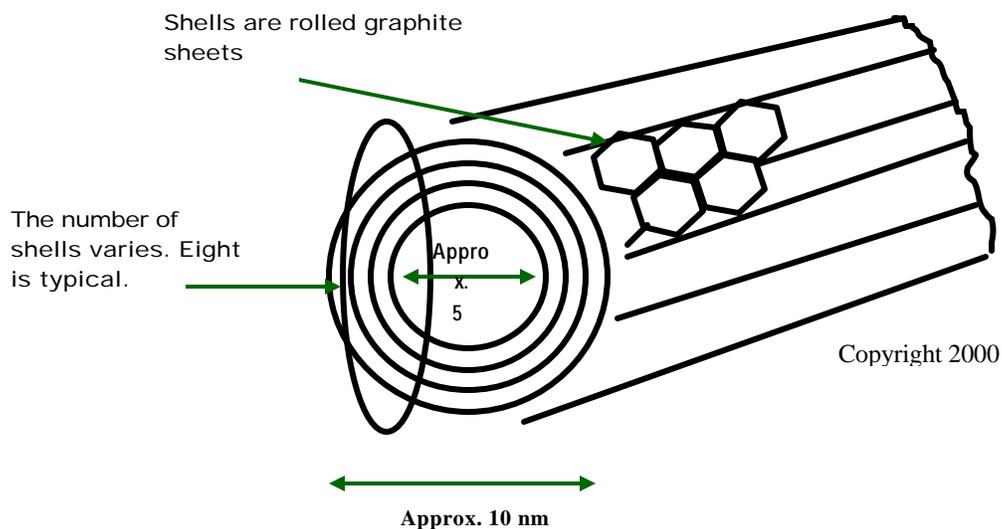
Figure 2. Photomicrograph Showing Nanotube Wall Structure
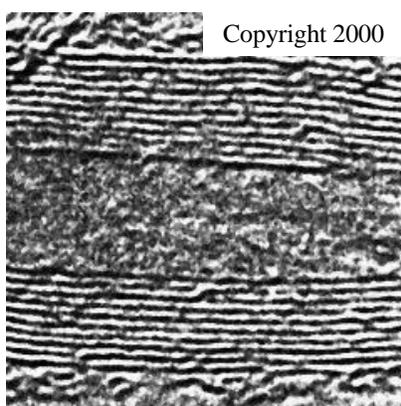
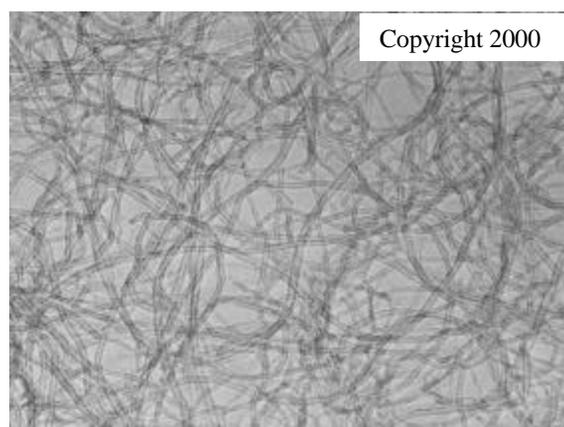Figure 3. Photomicrograph of Dispersed Nanotubes

Figure 6. Light Transmission Photomicrograph of Microtomed Section of Carbon Fiber-filled Injection Molded Bar
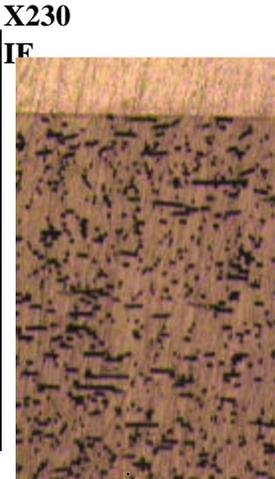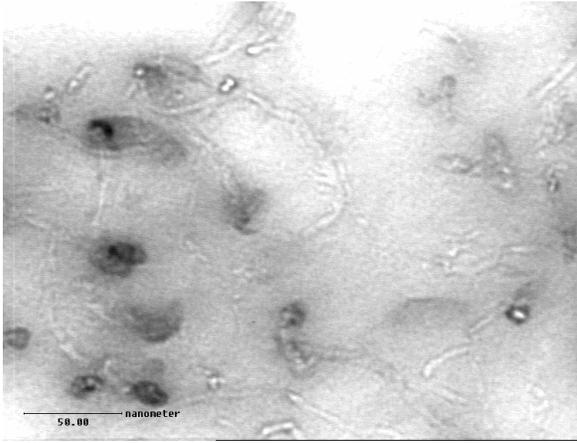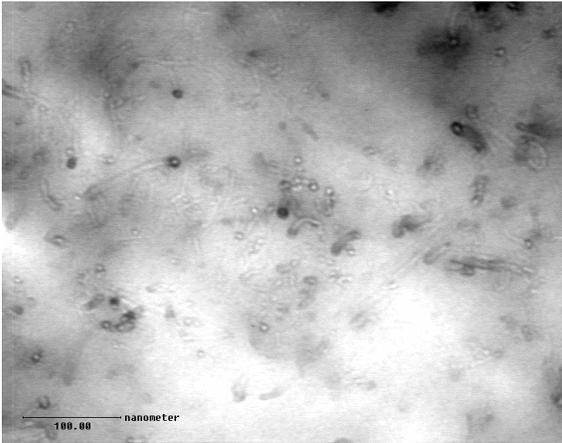
X230 Photo Courtesy of CRIF
IF

Figure 7. Transmission Electron Micrograph of Ultramicrotomed Section of Nanotube-filled Injection Molded Bar

Photos Courtesy of CRIF