CREATING HIGH PERFORMANCE CONDUCTIVE COMPOSITES WITH CARBON NANOTUBES

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Abstract

Multiwall carbon nanotubes are a very small, high aspect ratio conductive additive for plastics. The high aspect ratio means that a lower loading of nanotubes is needed compared to other conductive additives. This low loading preserves more of the resins toughness, especially at low temperatures, as well as maintaining other key performance properties of the matrix resin.

Introduction

Multiwall carbon nanotubes were synthesized in 1983 by scientists at Hyperion Catalysis International. These nanotubes are 10-12 nanometers in diameter and 10 or more microns long. They are made by a gas phase continuous reaction of low molecular weight hydrocarbons with a proprietary catalyst. Current production capacity using this process is in the multiple tens of tons, with the capability to readily expand to meet demand. Figure 1 is a drawing of the graphitic multiwall structure. Figure 2 is a transmission electron microscope image of a portion of a nanotube showing the multiwall structure surrounding the hollow core. Figure 3 shows the curvilinear structure of multiwall nanotubes. Figure 4 shows the relative size of nanotubes compared to carbon fiber or 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, as shown by Figure 5.

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).

Nanotubes Maintain More Ductility

Because of the different aspect ratios of the three additives, the level of additive required to obtain similar resistivities is different, see Table I. As seen in Table II, 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. 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.

Nanotubes Give Smoother Part Surface

Nanotubes have less of an effect on part surface quality because of their small size and low loading. 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 III shows the arithmetic average of the surface roughness.

Nanotubes Give Low Part Warpage

Nanotubes are much smaller than other particulate 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 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 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 IV shows the difference in shrinkage in the flow direction vs. shrinkage in the transverse direction for the three compounds. 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 Have Lower Effect On Viscosity

A fourth advantage of the low loading of nanotubes is that they do not raise the viscosity of the compound as much as the higher loading of larger fillers, as shown in Figure 8. This means that thin walled or large multi-gated parts may be more easily filled. Nanotube-filled plastics have been processed by all common techniques: injection molding, extrusion, blow molding and compression molding.

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, the low loading 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 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.

As the allowable losses of hydrocarbons have been reduced, the fuel lines have moved to a multi-wall construction using high barrier resins. ETFE is emerging as the barrier resin of choice in the N. American market, but in Europe there are a number of contending barrier resins including polyesters, EVOH, ETFE, PVDF and other fluoropolymers. Hyperion is developing compounds in these various resins, see Figure 9 for electrical percolation curves of selected nanotube filled compounds.

As N. American OEMs require more and more fuel system components to have ESD levels of conductivity, there is increasing interest in nanotube filled composites for pumps, filters, connectors, and fuel rails.

Another application area that has found success in Europe is thermoplastic fenders. In Europe, the high cost of fuel makes light weighting more important than in N. America. In addition, the strict recycle laws make thermoplastics more attractive than thermosets. 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. Having a conductive plastic is much preferred to spraying a conductive primer prior to the topcoats. The low loading and small size of carbon nanotubes allow an as-molded Class A surface while preserving more of the resin's ductility. This means the fender will not exhibit an undesirable brittle failure in a low temperature impact.

Acknowledgments

We would like to thank the Centre de Recherches Scientifiques et Techniques de L'industrie des Fabrications Metalliques (CRIF) in Belgium for conducting the comparative study of nanotubes, carbon black, and carbon fiber in PC/ABS and allowing Hyperion to use the data.

Figure 1. Structure of Multiwall Carbon Nanotubes

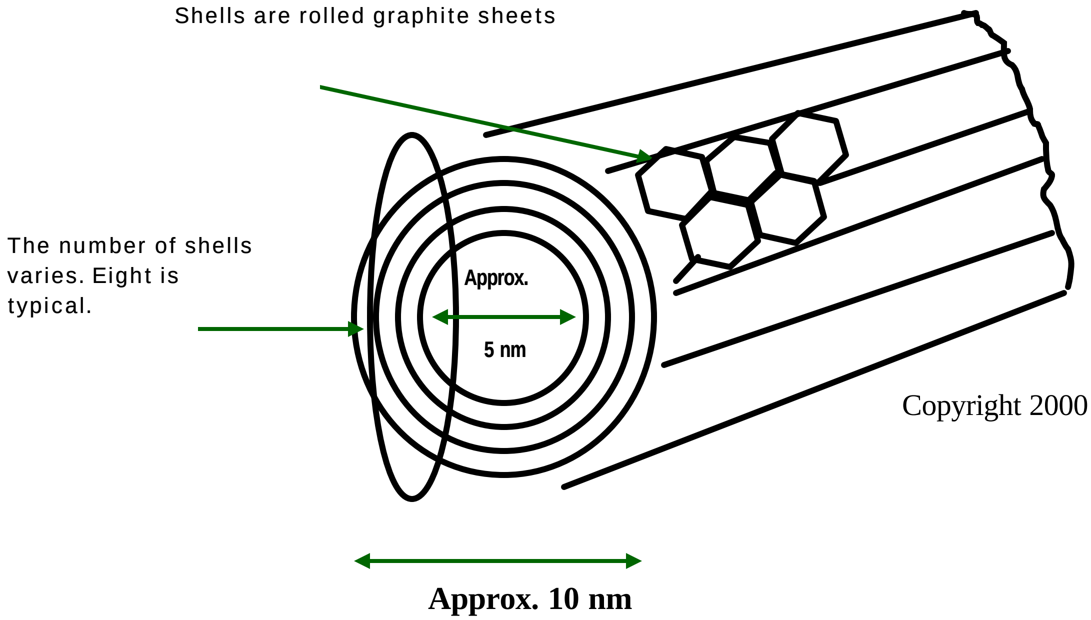

Figure 2. Photomicrograph Showing Nanotube Wall Structure

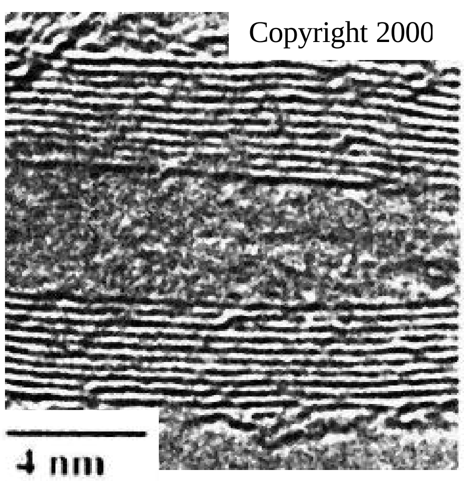

Figure 3. Photomicrograph of Dispersed Nanotubes

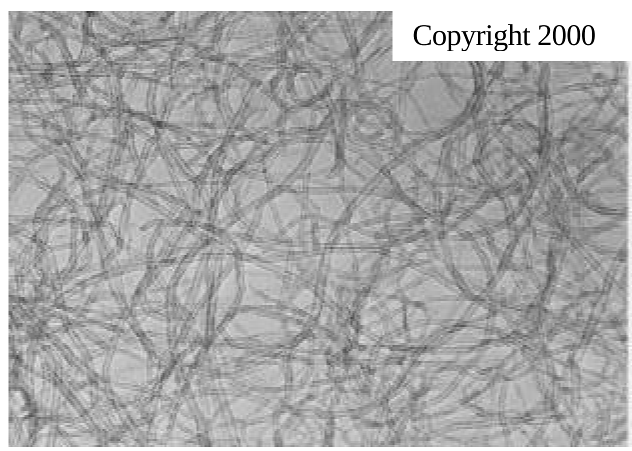

Figure 4: Comparison of nanotubes with carbon fiber and carbon black

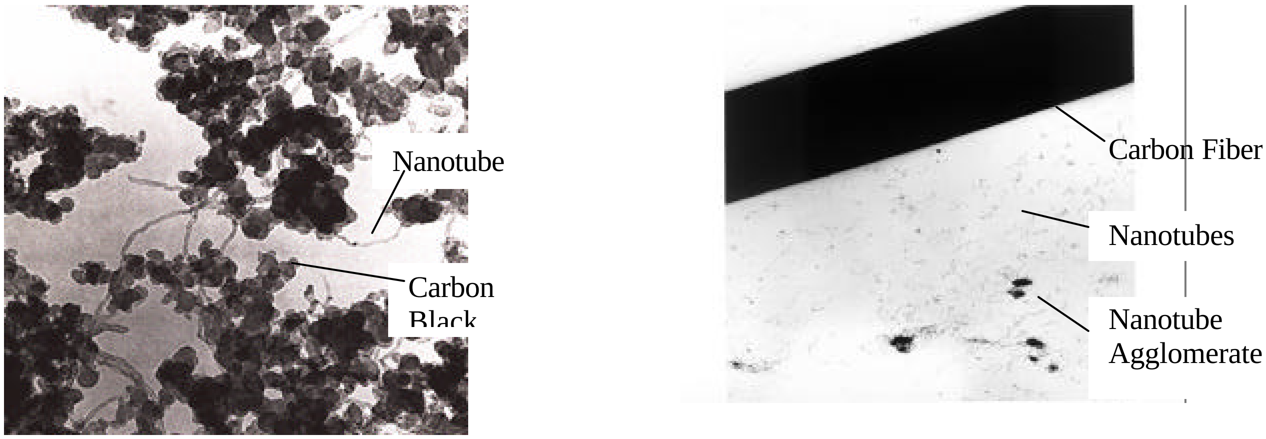

Figure 5. Calculated Loading for Percolation as a Function of Aspect Ratio

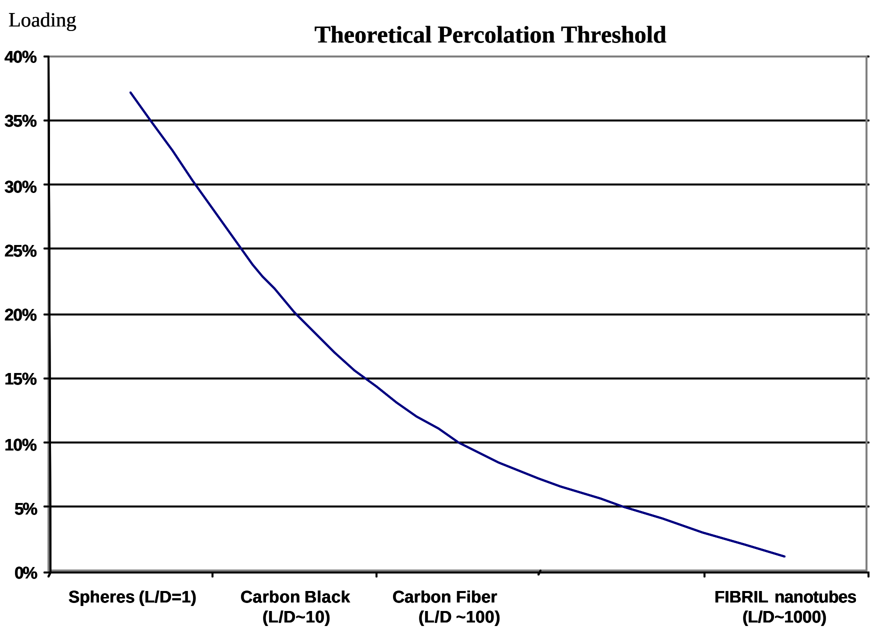

Table I. Resistivity vs. Additive/Loading in PC/ABS

Additive	Loading wt. %	Volume Resistivity (ohm-cm)	Surface Resistivity (ohms)
None		$10^{E}16$	n.a
Nanotubes	7.3	$10^{E}1$ - $10^{E}3$	$10^{E}4$ - $10^{E}6$
Carbon black	16.7	$<10^{E}3$	$<10^{E}6$
Carbon fiber	13.7	$<10^{E}3$	$<10^{E}6$

Table II. 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

Table III. 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

Figure 6. Light Transmission Photomicrograph of Microtomed Section of Carbon Fiber-filled Injection Molded Bar

X230 Photo Courtesy of CRIF

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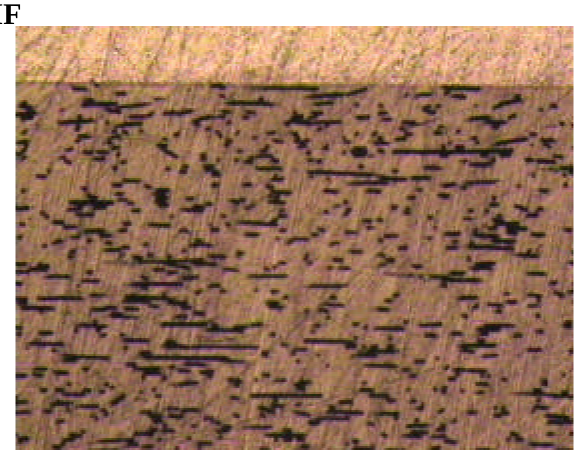
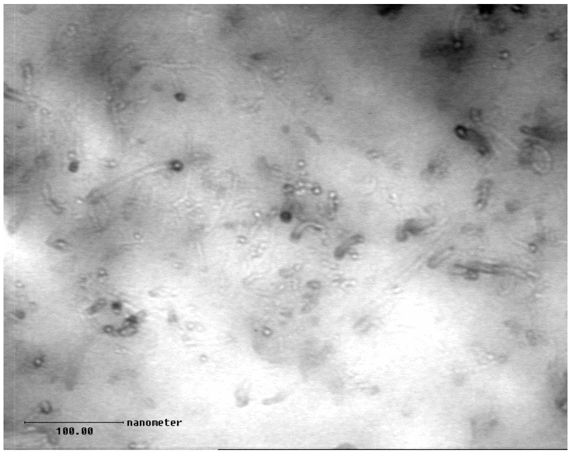


Figure 7. Transmission Electron Micrograph of Ultramicrotomed Section of Nanotube-filled Injection Molded Bar

Photos Courtesy of CRIF



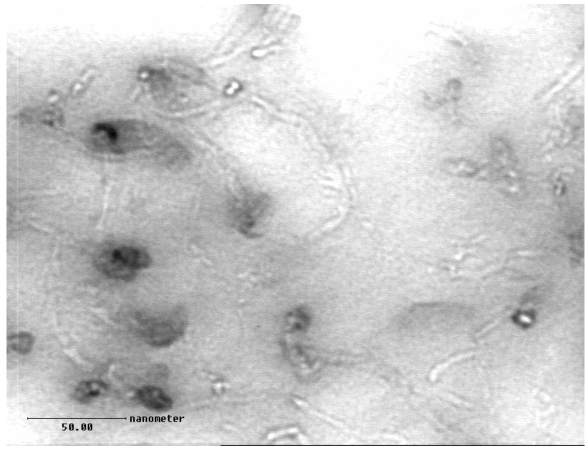


Table IV. Effect of Additive/Loading on Differential Shrinkage

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.

Fig. 8. Effect of Additive Loading on Resin Viscosity

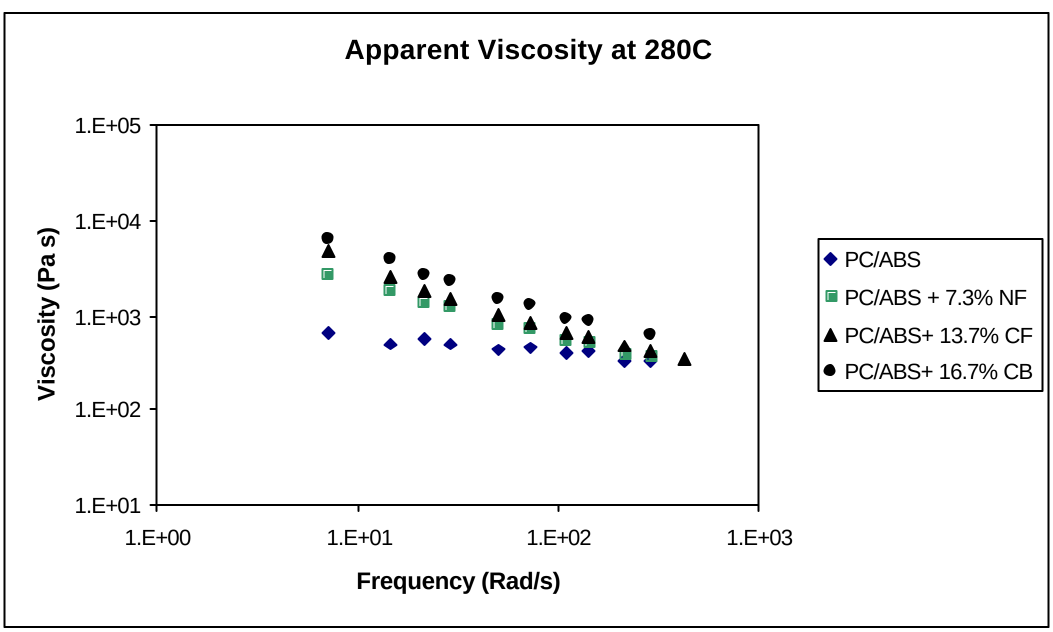
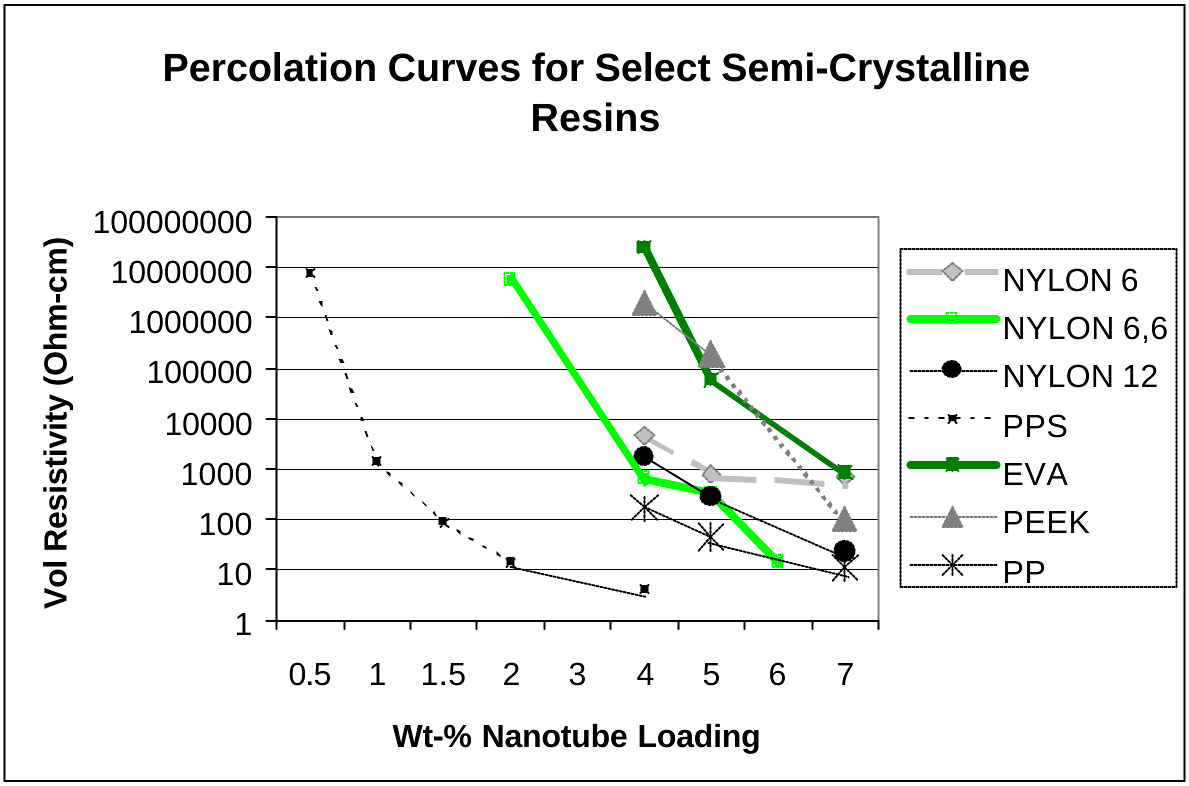
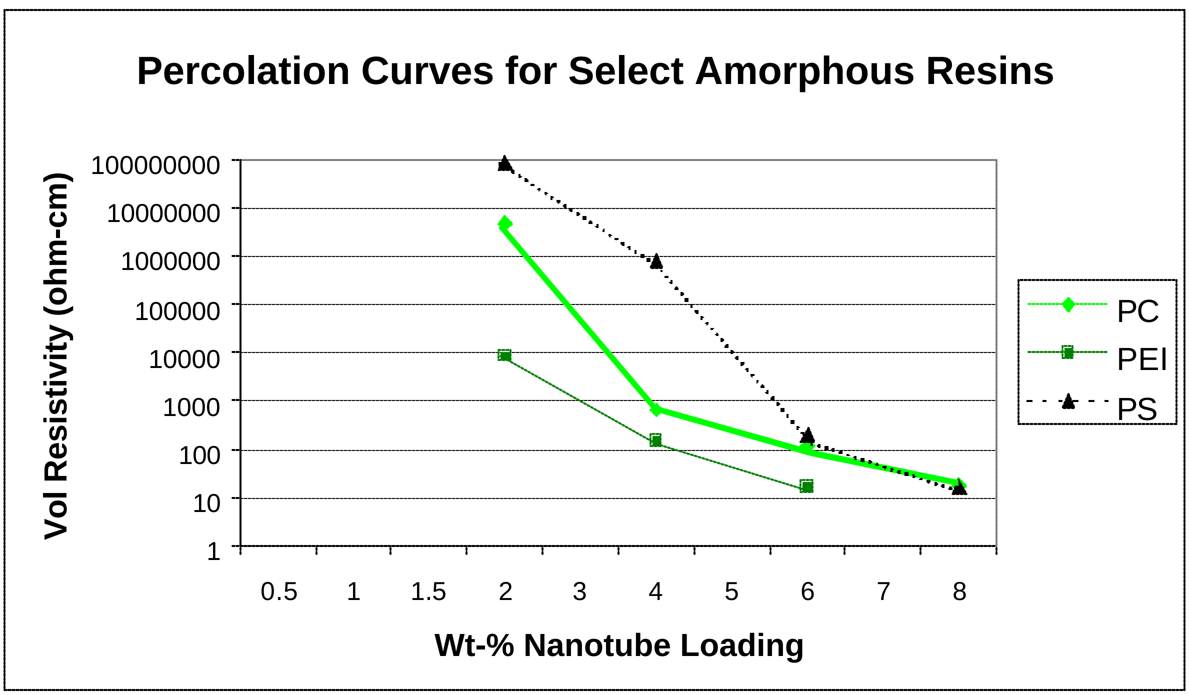
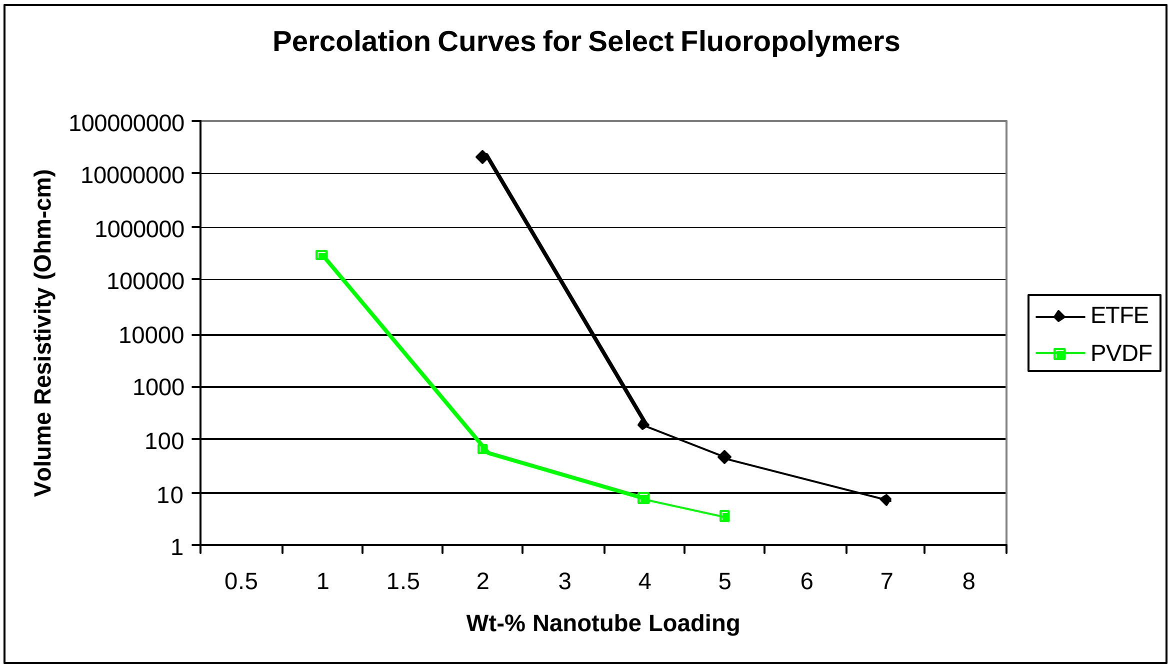


Fig. 9. Percolation curves for nanotubes in various polymers






Percolation Curves for Select Fluoropolymers
100000000
10000000
1000000
100000
10000
1000
100
10
1
Volume Resistivity (Ohm-cm)
0.5
1
1.5
2
3
4
5
6
7
8
Wt-% Nanotube Loading
ETFE
PVDF