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Nanotubes for Conductive Plastics Move to the Next Performance Level

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ABSTRACT

Multiwall carbon nanotubes are an extremely small conductive additive for plastics. They are about 10 nanometers in diameter and 10 or more microns long. Their high aspect ratio (1000:1) allows equivalent conductivity at lower loading compared to carbon black, chopped carbon fiber or stainless steel fiber. The advantage of a lower additive loading is a greater retention of the inherent ductility of the resin. Additionally, the small size of the nanotubes, coupled with the low loading, results in a much smoother molded part surfaces than when larger additives are used.

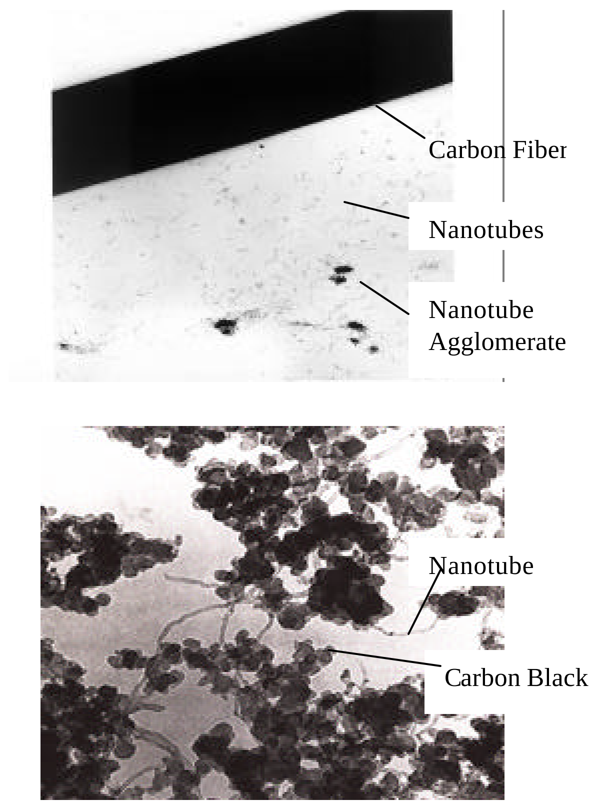
In this paper, we will present comparative data of physical properties, surface smoothness, moldability and electrical conductivity for compounds containing different conductive additives. Finally, existing and evolving commercial applications will be reviewed.

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 TEM of a portion of a nanotube showing the multiwall structure surrounding the hollow core, Figure 3 (Appendix) shows the curvilinear structure of multiwall nanotubes.

Carbon nanotubes have potential applications as catalyst supports, as cathodes in field emission displays and as electrodes, but the largest commercial application to date is as a conductive additive for plastics. Their high aspect ratio (1000:1) allows equivalent conductivity at lower loading compared to carbon black, chopped carbon fiber or stainless steel fiber, see Figure 4 (Appendix). Additionally, the small size of the nanotubes, coupled with the low loading, results in a much smoother molded part surface. Figure 5 shows the relative size of nanotubes compared to carbon fiber or carbon black.

Figure 5: Comparison of nanotubes with carbon fiber and carbon black



The small size of the individual nanotubes makes them very insensitive to shear fields and thus difficult to disperse. In addition, the as-made nanotubes intertwine into agglomerates (see Figures 5). Thus, in order to insure consistent, high quality dispersions, the initial dispersion of the nanotubes is typically done while making a master-batch of 15 to 20% concentration by weight. The masterbatch can then be let down, typically using conventional high shear compounding equipment, to insure good mixing between the high viscosity masterbatch and the lower viscosity let-down resin.

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 electrical resistivity. Because of the different aspect ratios of the three additives the required additive level is different to obtain similar resistivity, see Table 1.

Table 1. 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	<$10^{E}3$	<$10^{E}6$

ADDITIVE EFFECT ON RESIN DUCTILITY

An unfortunate consequence of the addition of particulate additives to most engineering resins is a decrease in resin ductility. While coupling treatments on fillers and additives have been found to reduce this effect, the coupling treatment tends to form an insulating layer around the additive, reducing the conductive effectiveness. Thus, conductive additives are almost always used without coupling agents. Table 2 shows the effect on resin ductility by the different conductive additives.

Table 2. Effect of Additive/Loading on Ductility

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

It can be seen that nanotubes lower the tensile elongation at break and un-notched izod much less than the carbon black or carbon fiber.

ADDITIVE EFFECT ON SURFACE SMOOTHNESS

Another unfortunate consequence of the addition of many particulate additives to thermoplastics is a decrease in the surface quality of the part. Because of their small size and low loading, nanotubes have less of an effect on part quality. Visual confirmation of this is shown in Figure 6 (Appendix). The number "5" was insert molded into plaques made from the different formulations. The photomicroscopic image of the feature on the plaque made with the nanotube compound is much sharper, it is easy to see that the curved part of the number is not continuous, but is made from a series of short, straight lines.

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

ADDITIVE DISTRIBUTION WITHIN PART

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 7 (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 8 (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. Since nanotubes are very much smaller than other additives they are much more insensitive to shear and thus form isotropic (random) distributions within molded parts. This insures a uniform level of conductivity throughout the most complex part or for large parts with multiple gates.

Another advantage of an isotropic additive distribution 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.

ADDITVE EFFECT ON RESIN VISCOSITY

Another issue with high loadings of conductive additives is an increase in polymer melt viscosity. In thin-walled parts or large parts with long flow lengths this can make molding very difficult. Figure 9 (Appendix) shows the apparent viscosity of the various compounds, it can be seen that the nanotube filled compound has the lowest viscosity over a wide shear range.

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 nantoubes 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 coextruded 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 wastful 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 exhibit ductile failure 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.

CONCLUSION

Carbon nanotubes are an extremely small, high aspect ratio form of graphitic carbon. They are an excellent conductive additive for thermoplastics in those applications where maintenance of ductility, surface quality and processability are important.

ACKNOWLEDGMENTS

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APPENDIX

Figure 1. Structure of Multiwall Carbon Nanotubes

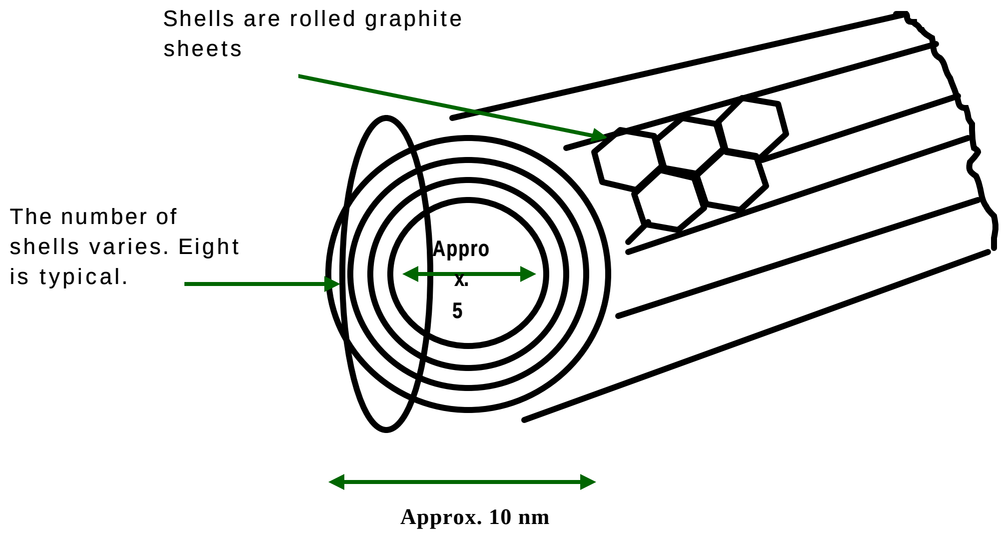

Figure 2. Photomicrograph Showing Nanotube Wall Structure

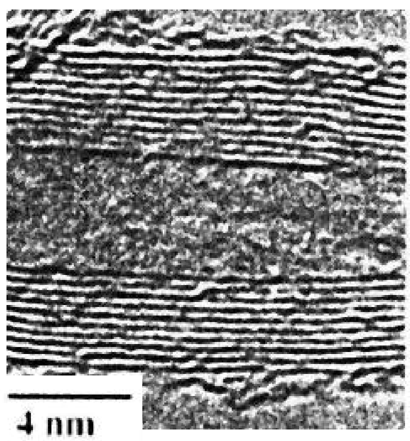

Figure 3. Photmicrograph of Dispersed Nanotubes

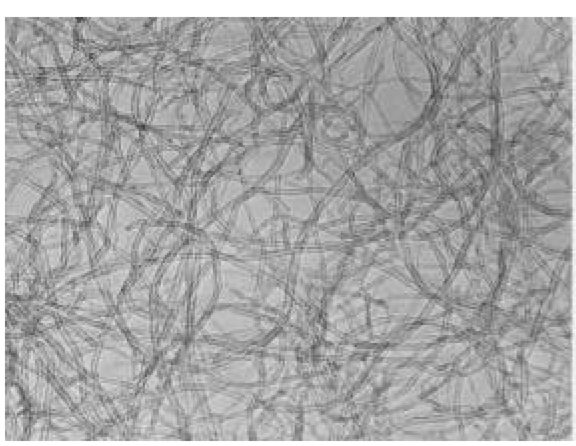

Figure 4. Calculated Loading for Percolation as a Function of Aspect Ratio

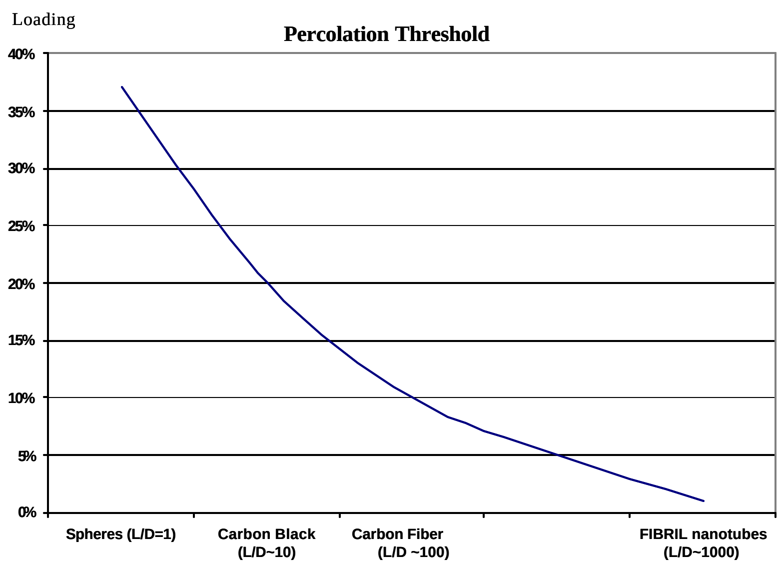

Figure 6. Surface Quality of Injection Molded Parts

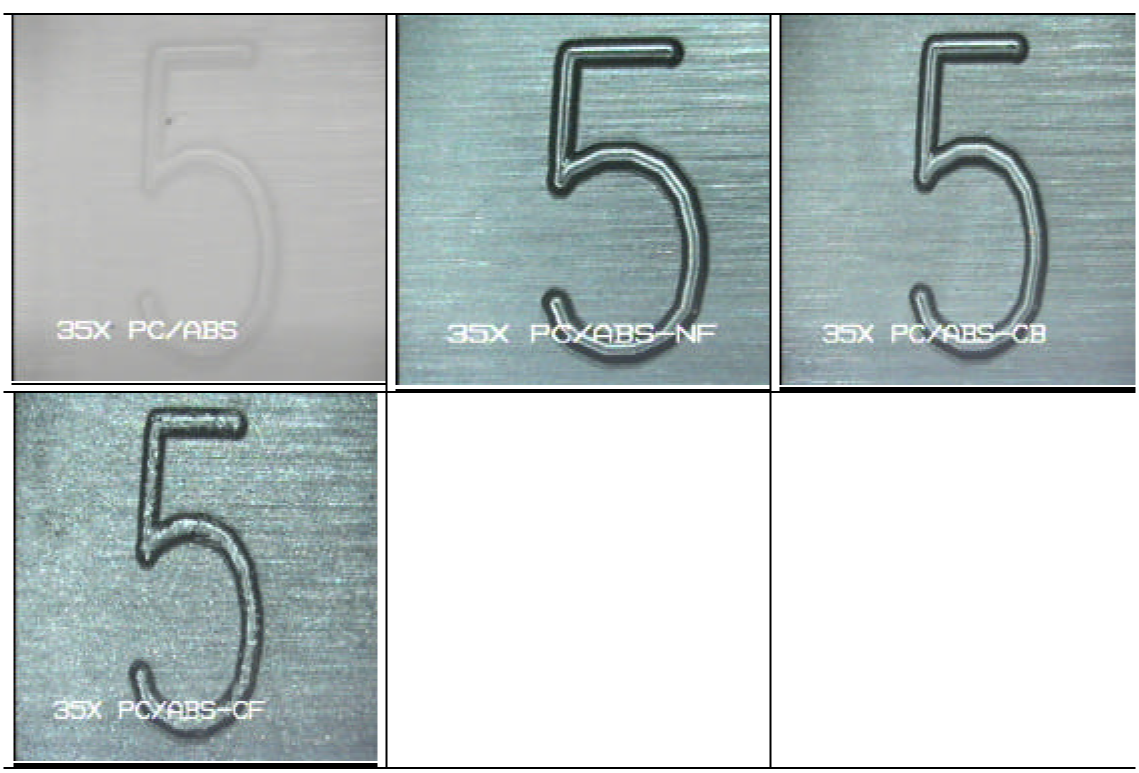

Figure 7. Light Transmission Photomicrograph of Microtomed Section of Carbon Fiber Filled Injection Molded Bar

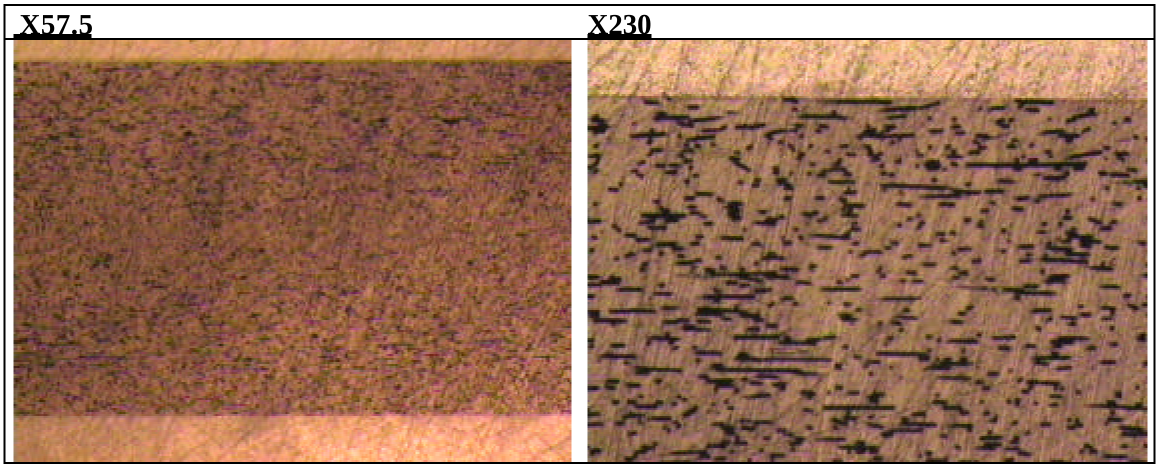

Figure 8. Transmission Electron Micrograph of Ultramicrotomed Section of Nanotube Filled Injection Molded Bar

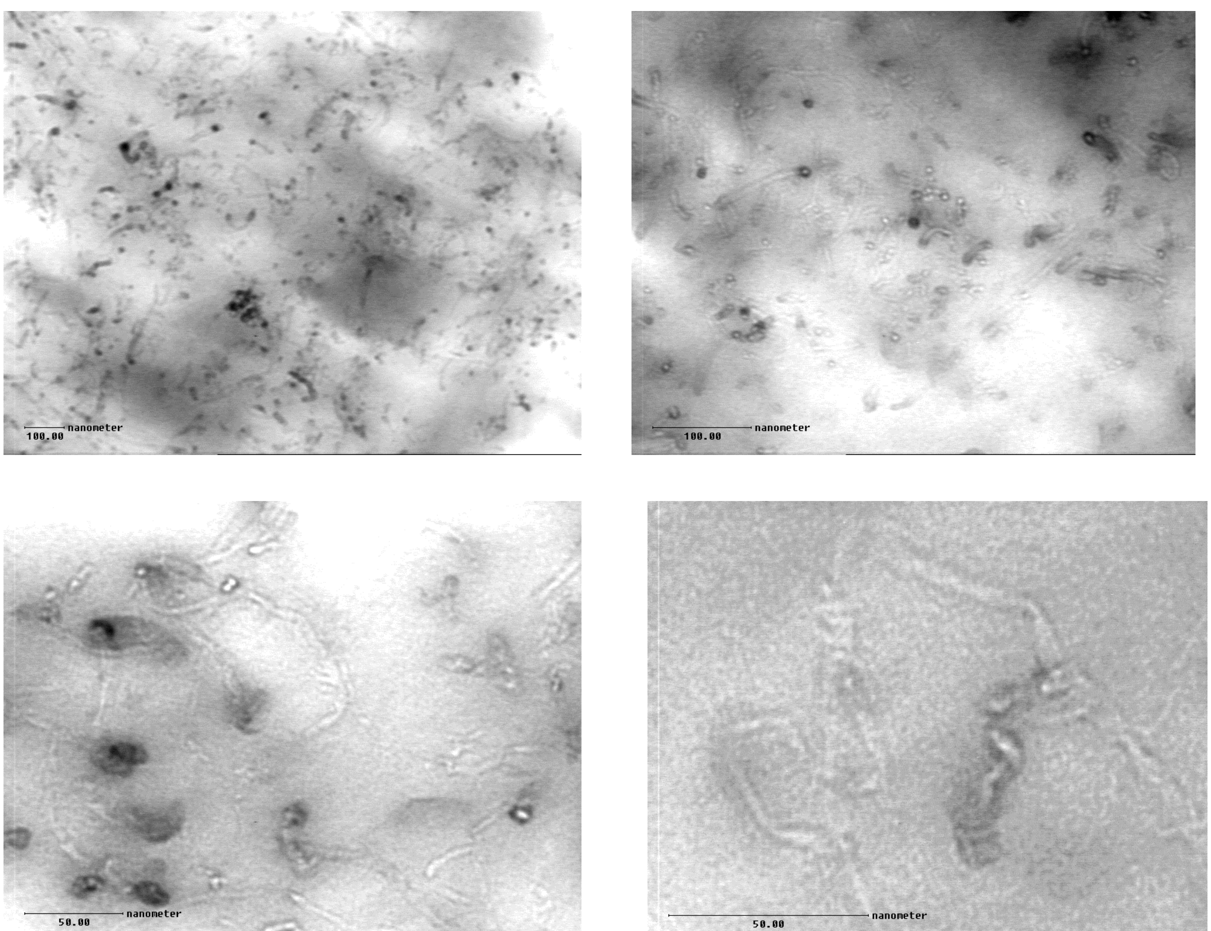

Figure 9. Apparent Viscosity of Conductive Compounds