

Carbon Multiwall Nanotubes as a Conductive or Flame Retardant Additive For Wire and Cable

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Abstract

Carbon multiwall nanotubes (CMWNT) are a relatively new and unique form of carbon. They are composed of concentric graphitic rings and are approximately 10 nanometers in diameter and 10 microns in length. They are currently in commercial use as a high performance conductive additive for plastics and are being investigated as a possible new, non-halogenated, flame retardant, especially in conjunction with nanoclays.

Keywords

Carbon nanotubes; conductive additive; flame retardant;

1. Introduction

Carbon multiwall nanotubes (CMWNT) have been in commercial use as a conductive additive for plastics only since the early 1990's. One new application that is being investigated is as a conductive additive in the strand and insulation shields for medium and high voltage power cable. Last year two groups showed that multiwall carbon nanotubes may be a non-halogenated flame retardant. Especially interesting was the observed synergy between nanotubes and nanoclays. This paper will review the nature of multiwall carbon nanotubes, give performance data on the use of nanotubes as a conductive additive, and give a brief introduction to their use as a flame retardant.

2. Characterization of Carbon Multiwall Nanotubes (CMWNT)

Carbon multiwall nanotubes were first synthesized in 1983 by scientists at Hyperion Catalysis International. These nanotubes are approximately 10 nanometers in diameter and 10 microns long. They are made by a continuous, catalyzed, high temperature gas phase reaction of low molecular weight hydrocarbons. Current production using this process is multiple tons, with the capability to readily expand to meet demand. Figure 1 is a representation of the graphitic multiwall structure

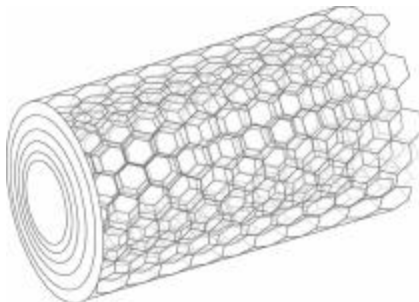


Figure 1. Graphic of CMWNT

Figure 2 is a transmission electron microscope image of a portion of a nanotube showing the multiwall structure surrounding the hollow core.

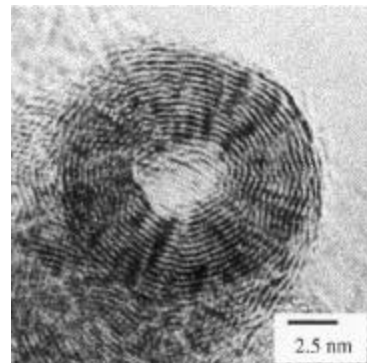


Figure 2. TEM end-on view of a CMWNT

Figure 3 is a scanning electron microscope image showing the curvilinear structure of multiwall nanotubes.

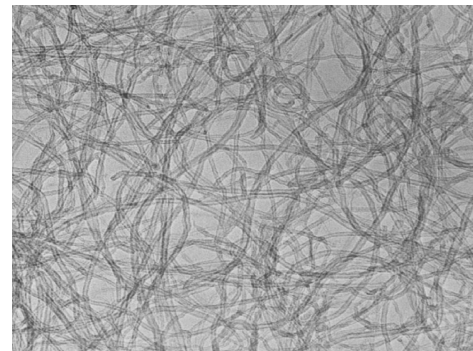


Figure 3. SEM of CMWNT

Carbon nanotubes have proven to be an excellent additive to impart electrical conductivity in plastics. Their high aspect ratio (length divided by diameter) of 1000 means that a very low loading is needed to form a percolating mixture in a polymer compared to materials with lower aspect ratios, such as carbon black, chopped carbon fiber, or stainless steel fiber, see Figures 4 and 5.

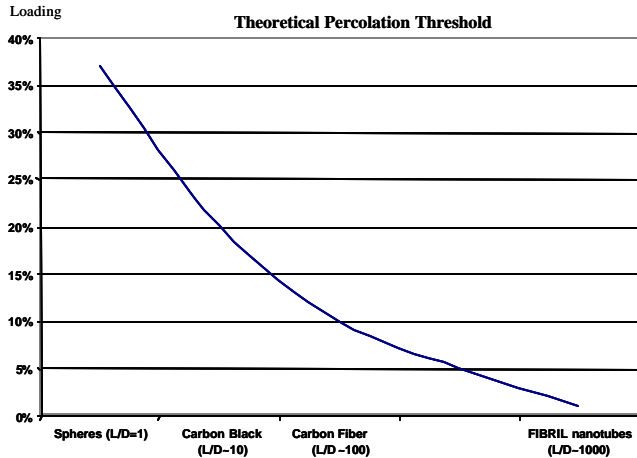


Figure 4. Effect of aspect ratio on percolation threshold loading

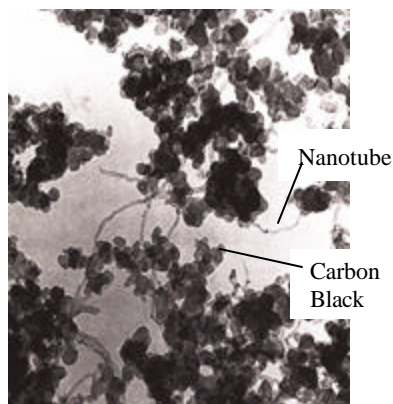
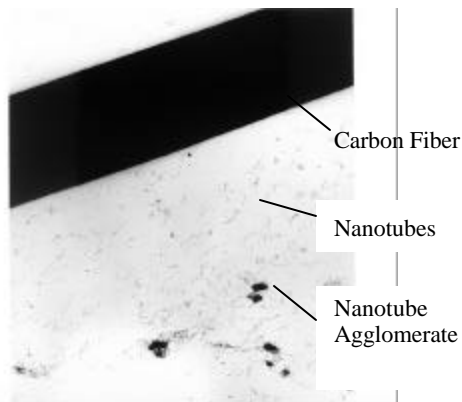


Figure 5. Relative size of CMWNT compared to carbon fiber and carbon black.

The benefits of lower loadings of conductive additives, on both polymer properties and polymer viscosity, will be discussed in the next section.

3. Performance of CMWNT as a Conductive Additive for Plastics

A study was completed in 2002 at CRIF in Belgium 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 surface resistivity. Because of the different aspect ratios of the three additives, the level of nanotubes needed to obtain similar resistivities is much lower, see Table 1.

Table 1. Loading of Various Additives Needed for Equal Resistivity

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

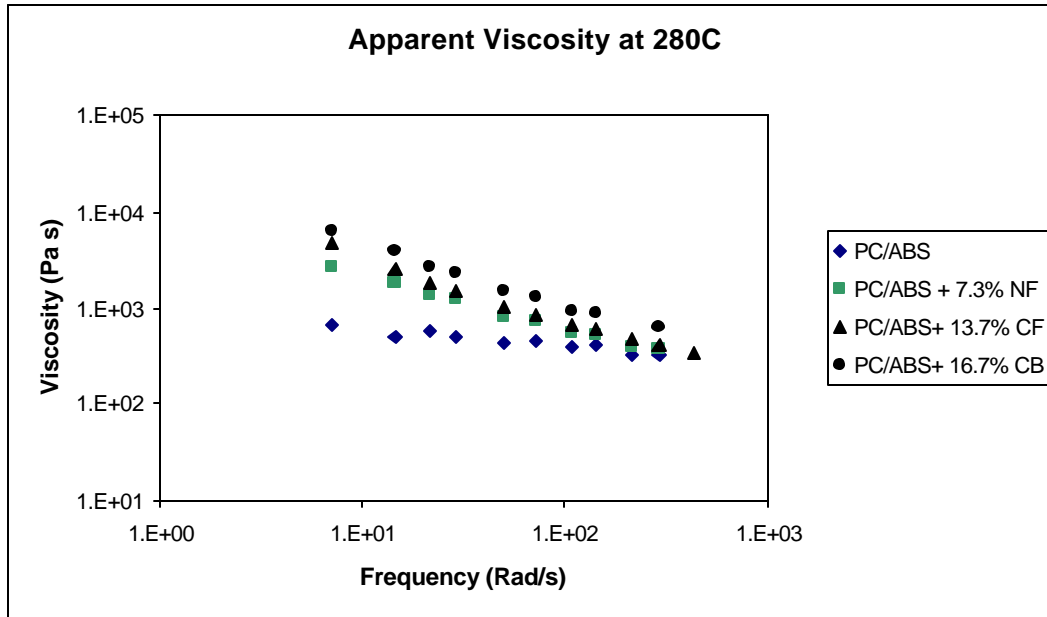
The addition of particulate additives to engineering resins frequently results in a decrease in resin ductility. This can be dangerous in applications where loss of resin toughness can hurt the performance of a part. The small size and low loading of nanotubes minimize the adverse effect on the ductility of the resin, see Table 2.

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

Another 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, see Figure 6. This means that thin walled or large multi-gated parts may be more easily filled.

Figure 6. Effect of Additive Loading on Resin Viscosity



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 and 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 of the compounds.

Table 3. Average Surface Roughness (Ra) vs. Conductive Additive

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

Carbon nanotube-filled plastics are being used in nylon 12 automotive fuel. Because moving fuel can build up a static charge, the fuel line needs to be conductive enough to bleed off the charge. The low loading of CMWNT preserves more of the tensile elongation of the resin and reduces the chance of a fuel line rupture in a low temperature accident. Additionally, the low loading of the very small nanotubes does not dilute the barrier properties of the resin to the permeation of gasoline vapor.

In the manufacture of semiconductor chips, the smallest static discharge can obliterate the small features that were so painstakingly photolithographically etched on the surface. During the manufacturing process, the wafers are transported from station to station in FOUPs (Front Opening Unified Pods)

have conductive plastic at all wafer contact points. In addition to being ESD conductive the part surface should be very smooth to prevent sloughing of particles as the wafers are inserted and removed from the FOUP. In the hyper-clean environment needed for chip manufacture, one free particle can destroy hundreds of thousands of dollars of product. The smooth surface that CMWNT provide are thus vital to this industry. 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, used in the manufacture of computer hard disc drives.

4. Performance of CMWNT as a Flame Retardant (FR) for Plastics

All plastics are based on hydrocarbons and nearly all are combustible. The control of plastic's combustion with flame retardant (FR) additives is essential in many industries such as aircraft, building/construction, public transport, and electrical/electronics equipment.

FR additives work by breaking one of the links that produce and support combustion: heat, fuel and air. The control of the toxic byproducts and smoke is also becoming a factor in assessing flame retardant additives. Increasingly, FR additives are used in combination, often with a synergistic effect.

The search for non-halogenated FRs has led to nanoclays, one nm thick by 1000 nm. diameter. Initial research showed that the addition of as little as 5% of nano-sized clay particles could produce a 63% reduction in the flammability of nylon 6. More recent studies have shown that flame retardancy in many other

polymers can be boosted by dispersing clay at the molecular level.

Two papers have been recently published on the use of multiwalled nanotubes as a flame retardant for plastics. G. Beyer [1] studied the effect of adding montmorillonite nanoclays modified with a quaternary ammonium compound and carbon multiwall nanotubes in ethylene-vinyl acetate (EVA).

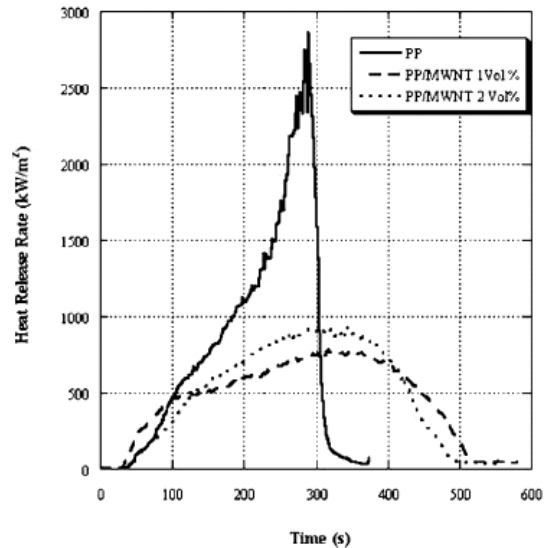
Beyer made several observations:

1. Nanotubes did not accelerate the time to ignition like the nanoclays (the clay's acceleration was attributed to the decomposition of the quaternary ammonium compound within the nanoclay.)
2. Nanotubes are better than nanoclays at reducing the peak heat release rate at either 2.4% or 4.8% loading. The char showed much lower crack density for nanotubes. The hypothesis is that the high aspect ratio of the nanotubes formed a reinforcing composite that made the char more resistant to cracking. The reduced cracking provided better insulation to the unburned polymer surface and hence reduced the emission of volatile gasses into the flame area.
3. An equal mixture of 2.4% nanotubes and 2.4% nanoclay gave a synergistic reduction in peak heat release rate. The char showed the least amount of cracking, due to the combined reinforcement effect of both fillers.

MWNT		Time to Ignition sec	Peak Heat Release Rate kW/m ²
%	Nanoclay %		
0	0	84	580
2.4	0	85	520
4.8	0	83	405
0	2.4	70	530
0	4.8	67	470
2.4	2.4	71	370

Kashiwagi [2] studied multiwall nanotubes in polypropylene (PP). A comparison of heat release rate curves among the three samples is shown in Figure 7.

Figure 7. Heat Release Rate for PP with CMWNT



The results show that the heat release rates of the PP/MWNT nanocomposites are much lower than that of PP even though the amount of CMWNTs in PP is quite small. This reduction in heat release rate is at least as much as what was previously found for clay nanocomposites in a maleic anhydride modified PP. Kashiwagi attributed the performance of the MWNT more to the presence of the small amount of iron catalyst in the MWNT. This iron may form iron oxides during combustion and iron oxides have been used as FR additives.

Another possibility that has been suggested is that the nanotubes function by conducting heat away from the flame zone. It is obvious that much work needs to be done to understand the mechanism.

5. Conclusions

Carbon multiwall nanotubes are a relatively new additive for plastics. They are being successfully used commercially as a conductive additive and may be a new, non-halogenated flame retardant that is effective in low loadings. As in the case with electrical conductivity the low loading would help to preserve more of the base resin properties.

6. 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.

7. References

- [1] G. Beyer, *Fire and Materials*, 26, (2002), 291-293.
- [2] T. Kashiwagi, et.al., *Macromol. Rapid Commun.*, 23, (2002), 761-765.