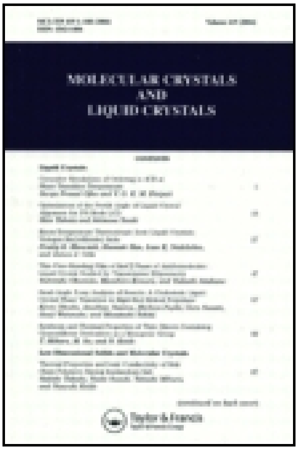

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Mechanical and electrical propertiesof vapor-grown carbon fiber thermoplastic composites

Gary G. Tibbetts [a], Ioana C. Finegan [a] & Choongyoong Kwag [a]
[a] Materials and Processes Laboratory, General Motors RD Center, Warren, MI, 48090, USA

Version of record first published: 18 Oct 2010

Mol. Cryst. Liq. Cryst., Vol. 387, pp. [353]/129–[357]/133

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113664

MECHANICAL AND ELECTRICAL PROPERTIES OF VAPOR-GROWN CARBON FIBER THERMOPLASTIC COMPOSITES

Gary G. Tibbetts, Ioana C. Finegan, and Choongyoong Kwag
Materials and Processes Laboratory, General Motors R&D Center, Warren, MI, 48090, USA

Vapor-Grown Carbon Fibers may be modified by surface or temperature treatment to be effective in reinforcing or adding conductivity to polymeric composites.

Keywords: vapor-grown carbon fibers; carbon nanofibers; composites; electrical conductivity

INTRODUCTION

Vapor-grown carbon fibers (VGCF) of about 200 nm in diameter may be used for many applications. Since their intrinsic modulus and tensile strength are high, they may be compounded with thermoplastics and used to form composites of good mechanical properties. Furthermore, since their intrinsic electrical conductivity approaches that of graphite, they may be used to make electrically conductive composites. Even though the constraints of inexpensive fabrication require that the composites be comprised of non-oriented fibers, yet good properties may nevertheless be obtained for both applications. In this paper we will show that relatively small quantities of VGCF can improve both the mechanical and electrical properties of thermoplastics.

Thanks to Robert Alig, Max Lake, and the staff of Applied Sciences for furnishing the fibers. Thanks also to NIST ATP, who supported Ioana Finegan and Choongyong Kwag under Cooperative Agreement Award No. 70NANB5H1173, *Vapor-Grown Carbon Fiber Composites for Automotive Applications*.

EXPERIMENTAL

The PYROGRAF VGCF were produced at the pilot plant of Applied Science, Inc., in Cedarville, OH. The fibers were formed by iron-based catalyst particles in a methane atmosphere [1] and were from 100–300 nm in diameter and many microns long.

The fibers were generally ball-milled for 2 minutes using a Spex 8000 mixer mill to improve resin permeation and injection molded in a benchtop CSI MiniMAX Molder using a cup temperature of 230°C. The mold was held at room temperature to inhibit crystallization. The following fiber designations refer to differing reactor gas mixtures used in production:

- In increasing order of gas space velocity: Clean, Best Shot.
- Acetylene-based fibers.

Other surface treatments used heat and oxidation:

- Graphitized fibers heated to 3000°C for 1 hour.
- Air-Etched fibers oxidized in air at 450°C.
- CO_2 oxidized fibers treated with CO_2 in a tube furnace at 850°C for 15 minutes.

During injection molding the mold was held at room temperature (23°C) for polypropylene (PP) resin to inhibit crystallization. The resulting specimens were mounted in the grips of an MTI tensile testing machine and were stretched at 1 mm/min until failure occurred.

MECHANICAL PROPERTIES

Figure 1 shows the tensile strength and stiffness for 15 volume % VGCF/polypropylene composites using fibers produced by these methods and having the various surface treatments described in the previous section. These data show that it is possible to triple both the modulus and strength of the polypropylene resin (open circle) by adding only 15 volume % VGCF. They also underscore the fact that some fiber production methods and surface treatments produce composites with much better properties than others. These results may be rationalized by the following two principles:

- Fibers grown under higher flow conditions tend to be more graphitic; with their shorter residence times they produce composites with poorer mechanical properties.

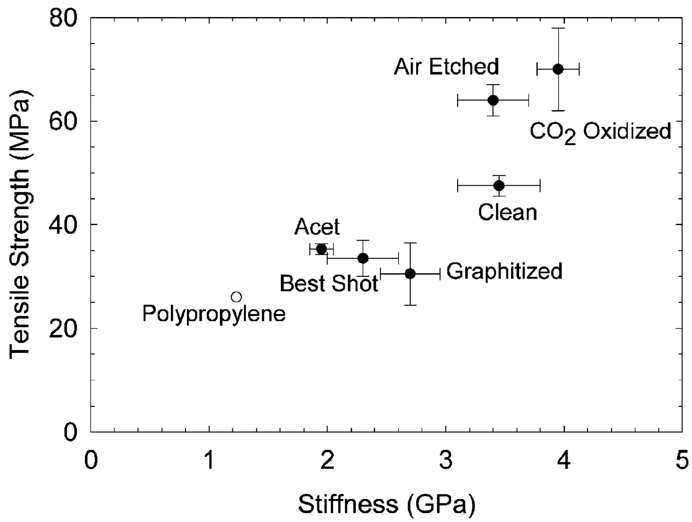

FIGURE 1 Tensile strength versus modulus for 15 vol% composites using different types of VGCF in polypropylene. The open circle shows the properties of polypropylene.

- A modest amount of oxidation of the surface increases the tensile strength of the composite, while too much etching can decrease it.

ELECTRICAL PROPERTIES

Figure 2 shows the approximate resistivities required for the more common applications for which electrically conducting plastics are sought: static dissipation, electrostatic painting with no primer coat, and radio frequency interference (RFI) shielding [2]. Figure 2 also exhibits resistivity Vs fiber volume fraction for "Clean" as-grown VGCF and two types of graphitized VGCF/Polypropylene composites: those prepared with and without ball milling. The latter are designated as "long graphitized". As the fiber volume fraction increases, the volume resistivity rapidly decreases for all of the composites. The percolation threshold is lowest for the long graphitized fiber and considerably higher for the "Best Shot" graphitized fiber. In agreement with the results of Gordeyev *et al.* [3], both types of graphitized VGCF/polypropylene composites have a significantly lower resistivity than the as-grown VGCF/polypropylene composites (87 Ohm cm) at 20% fiber volume fraction. The resistivity data points ρ are fitted to an expression derived from percolation theory, $\rho_0(V\text{-}V_c)^{-t}$, where ρ_0 is a constant scaling

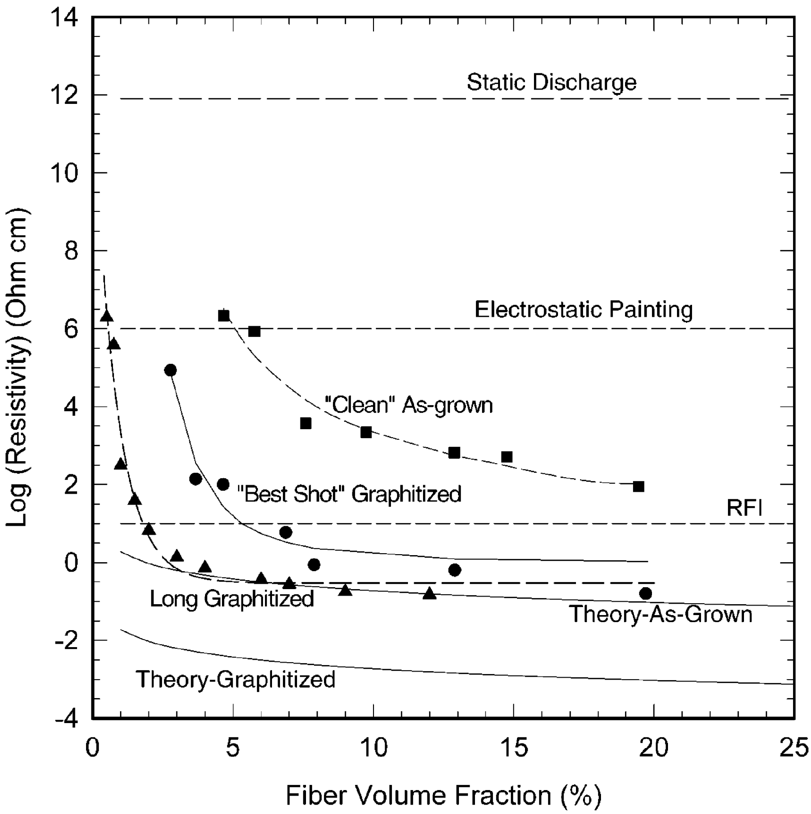

FIGURE 2 Approximate resistivity upper bound required for several applications, compared to electrical resistivity values measured for graphitized VGCF and clean VGCF in polypropylene.

factor, V the fiber volume fraction, V_c the critical volume fraction, and t the critical exponent.

Figure 2 also shows two calculated curves for the anticipated behavior of resistivity as a function fiber volume fraction for randomly oriented fibers in perfect contact [4]. These non-percolation calculations incorporate the electrical resistivity of 10 μm VGCF, heat treated to 3000°C, which have a room temperature resistivity very little larger than that of single crystal graphite, $6 \times 10^{-5}\,\Omega\,\text{cm}$ [5]. As-grown fibers that were produced at 1100°C have a much larger resistivity, measured to be $4 \times 10^{-3}\,\Omega\,\text{cm}$.

The electrical conductivity of VGCF/PP composites depends on the degree of graphitization and average fiber length. Composites made with 3000°C graphitized VGCF have lower resistivity than as-grown VGCF.

Those made with longer graphitized fibers have the lowest resistivity of all. After the sudden onset of electrical conduction with the addition of a few volume % of VGCF, the electrical resistivity monotonically decreases with fiber volume fraction, and the shape of this curve is consistent with classical percolation theory.

REFERENCES

[1] Tibbetts, G. G. *et al.* (1999). *Science and Applications of Nanotubes*, Tomanek, D. & Enbody, R. J. (Ed.), Kluwer: Netherlands, p. 35.
[2] Miller, B. (1996). *Plastics World*, September, 73.
[3] Gordeyev, S. A., Macedo, F. J., Ferreira, J. A., van Hattum, F. W., & Bernardo, C. A. (2000). *Physica B*, *279*, 33.
[4] Blythe, A. R. (1979). *Electrical Properties of Polymers*, (Cambridge, London), p. 126.
[5] Heremans, J. (1985). *Carbon*, *23*, 431.