Electrical Conduction in Vapor-Grown Carbon Fiber/Polypropylene Composites

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Introduction

Electrically conducting polymer-based composites are required in many applications, yet are difficult and expensive to make. Figure 1 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 [1]. The exact values required depend, of course, on the specific geometry of the pieces and the details of the application. In the following report, we will show that relatively small quantities of graphitized vapor-grown carbon fibers (VGCF) [2] can allow the fabrication of low resistivity composites of the thermoplastic polypropylene. The small fiber diameter of these VGCF makes these encouraging results possible.

Experimental

The fibers used in this study were produced at the pilot plant of Applied Science, Inc., in Cedarville, OH. They were approximately 200 nm in diameter and were formed by iron-based catalyst particles in a methane atmosphere [2]. Graphitized fibers were heated to 3000°C for 1 hour.

Both as-grown and graphitized fibers were ball milled to improve resin permeation for 2 minutes using a Spex 8000 mixer mill 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.

Results and Discussion

Figure 1 shows resistivity Vs fiber volume fraction for graphitized VGCF and clean VGCF/Polypropylene composites. Increasing the fiber volume fraction above 3% gives rapidly decreasing volume resistivity for the graphitized VGCF/polypropylene composites. The resistivity decreases from 7.9×10^4 Ohm cm at 3% fiber volume fraction to 1.5 Ohm cm at 8% fiber volume fraction, far below that required for static discharge protection or conducting primers. Moreover, the 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, $\rho_0(V-V_c)^{-t}$, where ρ_0 is a constant scaling factor, V the fiber volume fraction, V_c the critical volume fraction, and t the critical exponent.

Figure 1 also shows two calculated curves for the anticipated behavior of resistivity as a function fiber volume fraction for randomly oriented fibers in perfect contact [3]. 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, 6×10^{-5} Ω cm [4]. As-grown fibers that were produced at 1100°C have a much larger resistivity, measured to be 4×10^{-3} Ω cm.

Figure 2 shows the temperature dependence of the resisitivity of the 8 vol % graphitized VGCF/polypropylene sample. The resistivity decreases monotonically as temperature increases. This may be contrasted with the electrical resisitivity of the VGCF itself, which is metallic in nature [4] and increases with temperature. If there were perfect contact between fibers with no interfacial layer present, the conductivity would be described by the effective medium model of a percolation system. The decrease in resistivity with temperature T suggests that there is an energy barrier present at the fiber interfaces which electrons must surmount via a temperature activated process [15]. Furthermore, even for high fiber volume fractions the resisivity is still much higher than that of a single fiber.

Conclusions

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

The semiconducting or tunneling temperature behavior of the resistance with temperature indicates that conduction electrons must surmount an activation barrier between individual fibers. This behavior implies that the contact

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points between the fibers are the points of highest electrical resistance.

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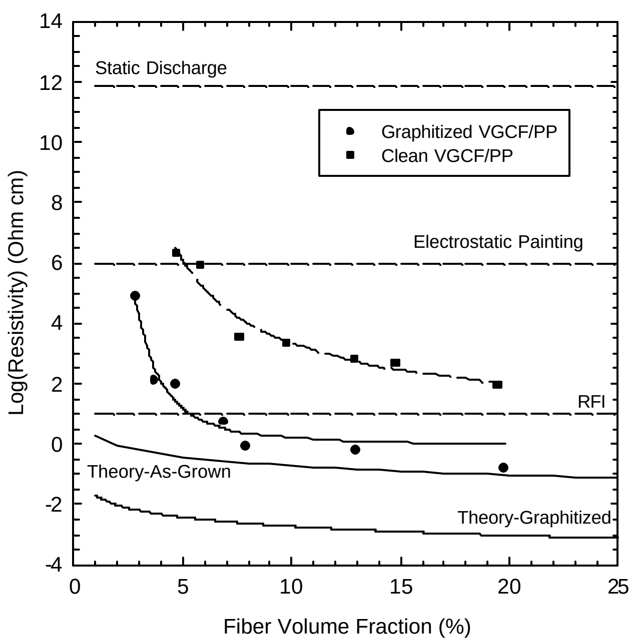

Figure 1. Approximate resistivity upper bound required for several applications, compared to electrical resistivity values measured for graphitized VGCF and clean VGCF in polypropylene.

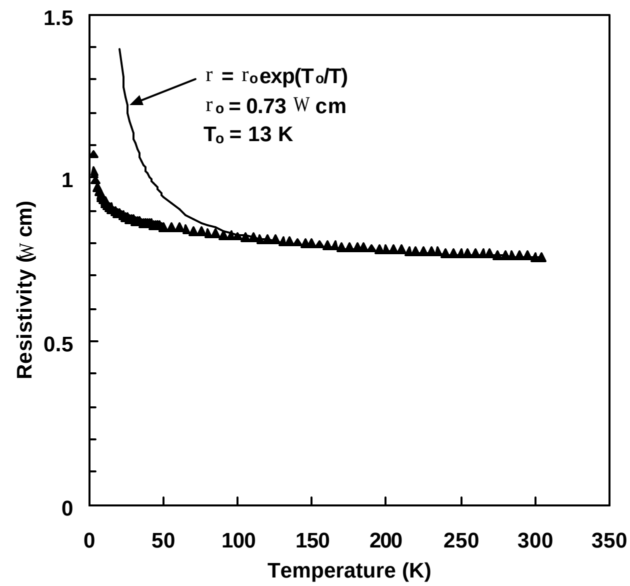

Figure 2 Resistivity of an 8 vol% graphitized fiber/PP composite vs temperature. Solid curve is a least squares fit to the resistivity equation shown in the plot.