HOW STRUCTURAL CHANGES INDUCED BY HEAT-TREATMENT OF CARBON NANOFIBERS CAN LEAD TO IMPROVED COMPOSITE PROPERTIES

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Introduction

Carbon nanofibers grown from iron catalyst particles may be used as fillers to add strength and stiffness [1] and electrical conductivity [2] to plastic materials. Because these fibers are, in varying degrees, graphitic [3], it would seem reasonable that their properties might be improved by graphitization heat-treatments. Indeed, we have shown that high temperature graphitization at near 3000°C can improve the electrical conductivity of composites fabricated from these fibers [2], although diminished adherence to polypropylene decreased the mechanical properties of their composites.

However, recent TEM studies [4] have shown that the morphological changes induced by this high temperature heat-treatment may be somewhat deleterious to the structural integrity of the fiber, and that a heat-treatment at intermediate temperatures may be more desirable. A preliminary investigation of the composite properties of our larger diameter fibers (~150 nm) showed that this was indeed the case [5]. This abstract details further work showing an optimal temperature of heat-treatment which optimizes the properties of polypropylene composites manufactured from lower diameter (~100 nm) fibers.

Experimental

The polypropylene (PP) used in this study was Montel Pro-Fax 6301 in flake form.

PYROGRAF fibers are 100-200 nm in diameter with an initial aspect ratio exceeding 100. Several varieties of fibers are produced by Applied Sciences, Inc., in Cedarville, Ohio (apsci.com) with different gas space velocities using various mixtures of feed gas. PR-24 fibers, (exclusively used in this study) are grown in a high velocity flow of methane, air, ammonia and the catalyst constituents hydrogen sulfide and iron pentacarbonyl. In general, they have a lower diameter than the PR-19 fibers we have previously described.

Because the as-grown fibers exit the reactor in large clumps, it is necessary to debulk the material to facilitate polymer infiltration. In laboratory-sized samples fabricated to measure mechanical properties, that is accomplished by ball-milling the fibers as we have previously described [1] for 2 minutes. We have shown that such debulking

diminishes electrical conductivity, so composites fabricated to measure conductivity use fibers that have not been ball-milled.

A bench-top CS-183 MiniMax Molder (Custom Scientific Instruments, Inc., Cedar Knolls, NJ, U.S.A.) was used for fabricating nanofiber/polymer composite specimens following a procedure we have previously described [1]. Resistivity measurements have also been previously described [2].

The fibers were loaded into graphite crucibles. The crucibles were opened when placed in the heat-treatment furnace and were purged by cyclic evacuation and backfilling with argon. The crucibles containing the sample fibers were heated to the target temperatures at a rate of 5 ˚C/min, and were held at the target temperature, determined by optical pyrometry, for one hour. The samples were then allowed to cool to room temperature over a 20-hour period.

Results

Figure 1 summarizes the results of many TEM studies of the heat-treated fibers, starting with a section of an as-grown nanofiber which has been exposed to a maximum temperature of 1150°C. At the bottom of the diagram is the fiber's hollow core. Above that is the inner core region, whose graphene planes have been formed catalytically by the Fe catalyst particle and are disposed at about a 25° angle to the longitudinal fiber axis. Above that is a region of vapor-deposited, turbostratic carbon of somewhat inferior crystallinity, manifested by a smaller crystallite size and larger 0001 d-spacing; these planes are oriented approximately parallel to the longitudinal fiber axis.

The center sketch represents a cross section of such a fiber after graphitization at 2900°C. The entire fiber has recrystallized onto the inner core planes in the "stacked cup" morphology, where the crystallite size is now much larger. The drawing on the right represents a fiber heated to 1500°C. At this intermediate temperature, the crystallite size and quality of the longitudinally disposed planes in the region of vapor deposited carbon have increased, but they are still longitudinal. Actual TEM's are shown in Figure 2.

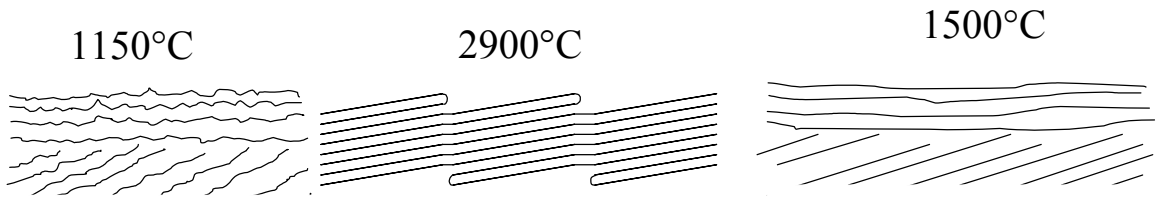

Figure 1. Morphological diagram drawn after TEM observations of an as-grown fiber, produced at 1150°C, and fibers heat-treated to 2900°C and 1500°C.

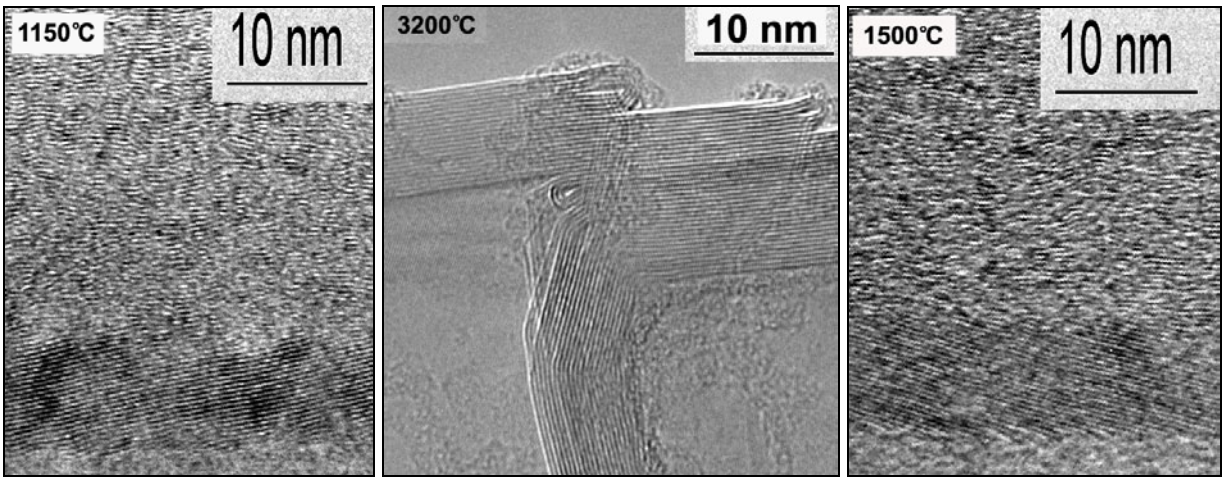

Figure 2. TEM images of fibers produced at 1150°C, and fibers heat-treated to 3200°C and 1500°C.

Figure 3 shows conductivity vs. volume fraction data for polypropylene composites of various volume fractions of nanofibers heat-treated at different temperatures. These conductivities manifest a maximum temperature near 1300°C, with a clear decline at higher temperatures.

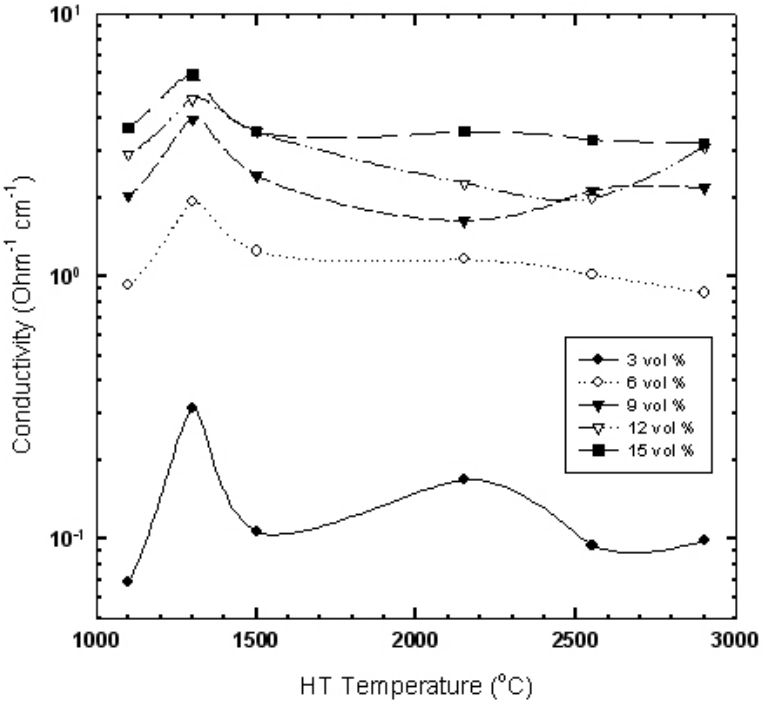

Figure 3. Conductivity of polypropylene composites made using various volume fractions of nanofibers heat-treated at high temperatures.

The mechanical properties of these composites are also optimized using fibers heat-

treated to intermediate temperatures. Figure 4 shows the tensile strengths of these composites.

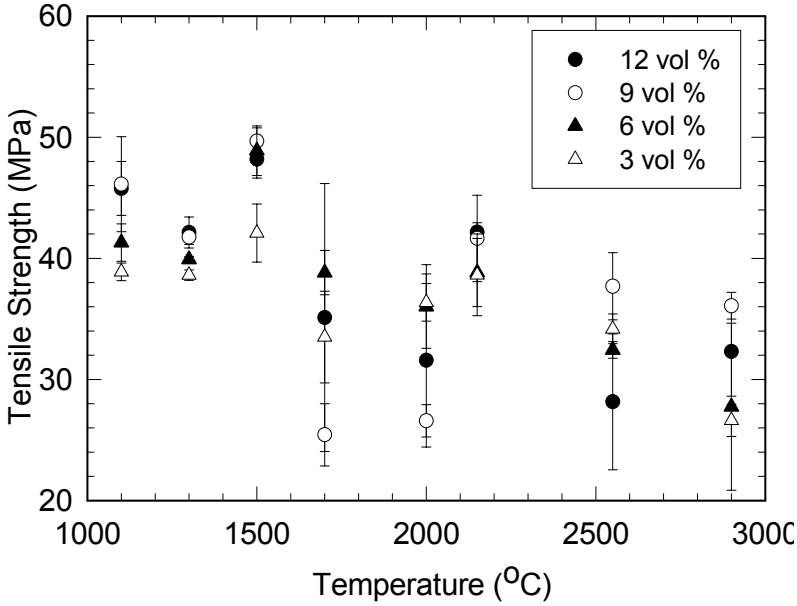

Figure 4. Tensile strengths of polypropylene composites made using various volume fractions of nanofibers heat-treated at high temperatures.

Discussion and Conclusions

Heat-treating carbon nanofibers having complex structures can lead to unusual and useful new morphologies. Our floating catalyst production process makes a carbon nanofiber with a hollow core surrounded by graphene planes oriented in a stacked-cup configuration. This structure is covered with vapor-deposited turbostratic carbon. Graphitizing at 2900°C results in the crystallization of the deposited layer of the nanofiber to the stacked-cup morphology. This complete crystallization diminishes the electrical conductivity and mechanical properties of composites manufactured from these nanofibers. Heat-treating to intermediate temperatures, however, first causes crystallites in the exterior deposited layer to increase their size and lattice coherence length parallel to the fiber axis. This crystal habit forms at heat-treatment temperatures between 1200 and 1600°C. Hence, an intermediate stage of graphitization can yield a fiber with optimum longitudinal properties. Polypropylene composites fabricated from these heat-treated nanofibers show the beneficial effects of this intermediate temperature heat-treatment; they are manifested in improved composite electrical conductivity and strength.

Acknowledgment

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