

Fibers from polypropylene/nano carbon fiber composites

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Abstract

Fibers from polypropylene and polypropylene/vapor grown nano carbon fiber composite have been spun using conventional melt spinning equipment. At 5 wt% nano carbon fiber loading, modulus and compressive strength of polypropylene increased by 50 and 100%, respectively, and the nano carbon fibers exhibited good dispersion in the polypropylene matrix as observed by scanning electron microscopy. © 2002 Elsevier Science Ltd. All rights reserved.

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The average diameter of vapor grown nano carbon fibers bridges the gap between those of conventional carbon fibers (7–10 μm) and of single wall carbon nanotubes (SWNT) (~ 1 nm) and multiwall carbon nanotubes (MWNTs) (2–50 nm). While SWNTs have unique properties [1], they have been produced in limited quantities to date and are expensive. Vapor grown nano carbon fibers, on the other hand, can be produced today in high volumes at low cost, using natural gas or coal as feedstock [2,3]. Nano carbon fibers have typical diameters of 50–200 nm, inner diameters or a hollow cores of 30–90 nm, and lengths in the range of 50–100 μm [2]. Aspect ratios (length to diameter ratio) in the 100–500 range are therefore typical with such geometries.

Reinforcement of polymer and other matrix systems with single and multiwall nanotubes, as well as with nano carbon fibers have been previously demonstrated to increase physical properties of the matrix materials. Such studies include pitch/SWNT composite fiber [4], polystyrene/MWNT [5], PVA/MWNT [6], PMMA/SWNTs [7] poly (hydroxy-aminoether) (PHAE)/MWNTs [8] and polypropylene/MWNTs [9]. In general tensile modulus and glass transition temperature are reported to increase with the presence of carbon nanotubes. In epoxy/MWNT, it was observed that the compression modulus (4.5 GPa) was higher than the tensile modulus (3.7 GPa)[10]. To explain this difference in modulus, it was proposed that during load transfer to multiwall nanotubes, only the outer layers are stressed in

tension whereas all the layers respond in compression [10]. Based on the fragmentation test, the interfacial strength in a MWNT/polymer system (urethane-diacrylate oligomer) was estimated to be 10 times that of a typical polymer/carbon fiber composite, and the compressive strength of MWNTs has been estimated to be 150 GPa [11]. This compressive strength is an order of magnitude higher than that of any other known material [12,13]. Wetting of nanotubes by polymer and nanotube pullout have been observed [14]. The onset of buckling and fracture strains in MWNTs were estimated to be ~ 5 and $>18\%$, respectively [14]. Measurements of tensile strength (1.72 GPa) and tensile modulus (450 GPa) of MWNTs themselves have also been reported [15]. Nano carbon fiber composites have been processed using a variety of matrices, including polypropylene [16], polycarbonate [17], nylon [18], and poly(phenylene sulfide)[19]. In this paper, we report the processing, structure, and properties of fibers from PP/vapor grown nano carbon fiber composites. For general fiber processing technology, reader is referred to a recent text in the field [20].

Vapor grown nano carbon fiber—Pyrograf III (PR-21-PS) was obtained from Pyrograf Products Inc., Cedarville OH. A scanning electron micrograph of the as received nano carbon fibers is given in Fig. 1. Polypropylene powder (#107200P; Melt Flow Index of 17) was received from Amoco Co. As received polypropylene (95 g) and nano carbon fibers (5 g) were mixed prior to being fed to a Haake rheocord 90 twin-screw extruder (TW-100). Temperatures in the four extrusion zones were 150, 220, 220, and 240 °C (exit zone) and the extrusion speed was

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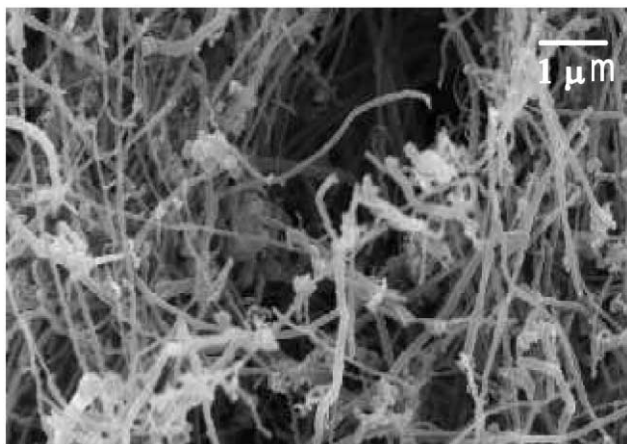


Fig. 1. Scanning electron micrograph of nano carbon fibers (Pyrograf III—PR-21-PS).

~20 rpm. Extruded material was quenched in a water bath (at room temperature) and subsequently palletized and dried under vacuum at ~80 °C for at least 12 h. The extruded material was spun using a small-scale (~50 g quantity) fiber spinning unit manufactured by Bradford Research Ltd UK, using a 600 μm diameter spinneret. Fiber spinning was carried out at 240 °C and at 30 m/min. Extruded strands were subsequently drawn (draw ratio 4) on a hot plate at 130 °C. Diameter of the drawn fiber was 55 μm. As a control sample, as received polypropylene without nano carbon fiber was also spun using the same equipment and processing conditions.

Fiber tensile properties were measured on 2.54 cm gage length samples using an Instron tensile tester (model 5567) at a cross-head speed of 12.5 cm/min. Fiber diameters were measured using laser diffraction. Compressive strength was determined using the loop test [21]. Tensile data is reported for an average of 25 tests while compressive data is reported for an average of 10 tests. Scanning electron micrographs were obtained using either a Cambridge stereoscan or Hitachi S-800 SEM. For SEM examination, fiber samples were sputter coated (~10 nm thickness) with gold. A laser scanning confocal microscope [LSCM] (Leica DMRBE) was used to study the macroscopic structure of the fibers.

Properties of the control and the composite fibers are given in Table 1. Based on this data it is clear that the composite fibers have higher modulus and compressive strength as compared to control PP fibers. While tensile strength was not significantly affected, strain to failure was observed to decrease as a result of filling with the nano carbon fiber. Based on the rule of mixtures and the

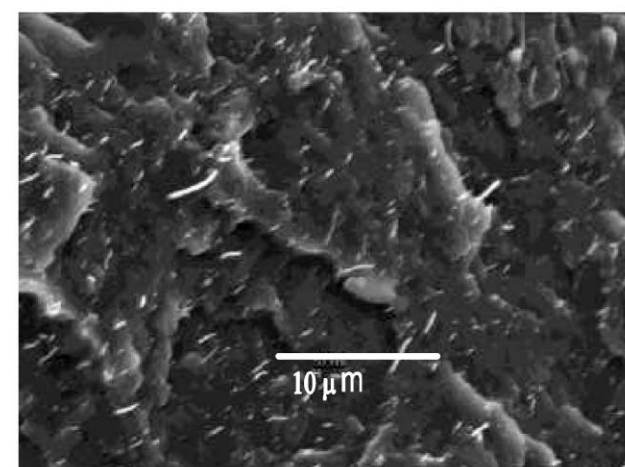
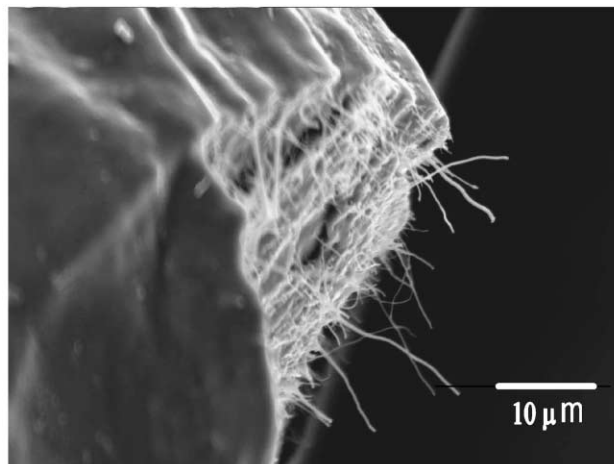


Fig. 2. Scanning electron micrographs of fibers from PP/nano carbon fiber composite.

moduli of nano carbon fiber (450 GPa) and PP fiber (5 GPa), a modulus value of approximately 17 GPa would be predicted for the composite fiber containing 5 wt% (~2.8% by volume) nano fiber, assuming perfect orientation for the nano fibers in the composite fiber. Scanning electron micrographs (Fig. 2) show good dispersion of the nano carbon fibers in the spun fibers. The images taken with the confocal microscope demonstrate that the layer close to the skin (Fig. 3a) appears to have fewer nano fibers, while having a higher degree of orientation of the carbon nano-fibers. In the layer farther away from the 'skin', the carbon nanofibers seem to be more aggregated (Fig. 3b) than those at the skin of the fiber. However, it does appear that there is little evidence of very large aggregates in the fiber formed. The dark lines that are visible in the micrographs may be

Table 1
Properties of fibers from polypropylene and PP/nano carbon fiber composite

Sample	Tensile strength (MPa)	Tensile modulus (Gpa)	Elongation to break (%)	Compressive strength (MPa)
PP-control	490 ± 60	4.6 ± 0.7	23 ± 5	25 ± 1
PP + 5 wt% nano carbon fiber	570 ± 70	7.1 ± 0.9	16 ± 2	48 ± 10

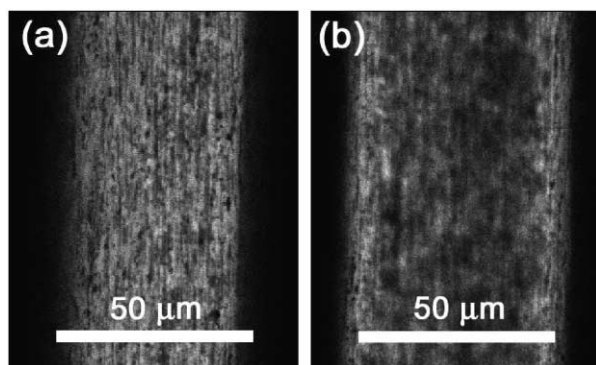


Fig. 3. Laser scanning confocal microscope images of PP/nano carbon fiber; (a) at 3.6 μm and (b) at 7.2 μm below the fiber skin.

diffraction limited images of the vapor grown carbon nano-fibers, since their diameters are too small to be resolved with the optics of a confocal microscope. In wide angle X-ray diffraction, polypropylene (060) and graphite (002) reflections overlap and full width at half maximum for a combination of these reflections was 6.8° , suggesting high degree of orientation for both the polypropylene as well as nano carbon fibers.

In conclusion, we have demonstrated that fibers from PP/nano carbon fiber composites can be spun using the conventional melt spinning equipment and possess superior modulus and compressive strength at 5 wt% loading of nano carbon fiber. It is also apparent that good dispersion of the nano carbon fiber was obtained by melt processing in polypropylene matrix as demonstrated by the SEM and LSCM images. While the observed fiber moduli have improved significantly (50%) by reinforcement with the nano carbon fibers, rule of mixtures calculations suggest that further improvements in modulus are likely, if perfect alignment and perhaps better interfacial adhesion of nano carbon fibers could be achieved in the polypropylene matrix fiber. Work

in progress will attempt to perfect nano carbon fiber alignment in the polymer matrix, as well as to extend this study to poly (ethylene terephthalate), nylon and PMMA fibers.

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