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Processing and mechanical performance of liquid crystalline polymer/nanofiber monofilaments

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Monofilaments of Vectra A950, a thermotropic liquid crystalline polymer, with 0–10 wt.% of vapor-grown carbon nanofibers were extrusion-mixed and characterized by tensile testing, nanoindentation and fractography. A maximum increase in modulus (35%) and strength (18%) was observed at the 1–2% nanofiber level, and increases were observed with decreasing diameter for all nanofiber concentrations. Incomplete dispersion of nanofiber clumps and microvoiding are thought to be responsible for the observed decrease in property values at the higher nanofiber levels.
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Vectra is a family of commercial thermotropic liquid crystalline polymer (LCPs) with rod-like molecules that align in nematic mesophase regions from the melt state [1]. Extensional flow (e.g. during extrusion) results in significant orientation of the nematic regions along the direction of flow [2], which yields higher mechanical strength and modulus [3]. Vectran-UM yarn (monofilament diameter 23 μm), for example, exhibits modulus and strength of 103 and 3 GPa, respectively [4]. Pyrograf III is a family of commercial vapor-grown carbon fibers (VGCF) with a hollow graphitic core and diameters ranging from 70 to 200 nm. Pyrograf III has been added to polymers to enhance conduction (electrical, thermal) and mechanical performance [5]. In a recent work, interactions between nanofibers (similar to VGCF) and Vectran V400P grade LCP have been studied via X-ray, conduction and mechanical property measurements [6].

The primary goal of our work is to explore the role of interactions between the LCP nematic zones and VGCF in the enhancement of mechanical properties. In this paper, we report on a study of extruded monofilaments of Vectra A950 LCP blended with VGCF. Monofilaments with diameters ranging from 1.2 to 1.9 mm have been tested to determine their elastic modulus and ultimate strength. Nanoindentation has been used to examine modulus and hardness variations across the monofilament cross-section. Optical microscopy and scanning electron microscopy (SEM) have been used to characterize the as-received VGCF and post-extrusion LCP–VGCF fracture morphologies. A maximum increase in modulus (35%) and strength (18%) was observed at the 1–2% VGCF level, and increases in modulus and strength were observed with decreasing diameter for all VGCF concentrations. Incomplete dispersion of VGCF, microvoiding, and possible orientation interactions between the VGCF and LCP nematic zones are thought to be responsible for the observed decrease in properties at higher VGCF levels.

Vectra A950 LCP, an aromatic main-chain copolyester composed of 73 mol.% 4-hydroxybenzoic acid (HBA) and 27 mol.% 6-hydroxy-2-napthoic acid (HNA) [7], was supplied in the form of pellets (~2 mm diameter and ~3 mm long) by Ticona, USA. Pyrograf III VGCF, type PR-24 and grade HHT, is an iron-free

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graphitized nanofiber supplied by ASI/Pyrograf Products Inc., USA. Fiber diameters range from 70 to 200 nm.

LCP pellets and VGCF in ratios corresponding to 1, 2, 5 and 10 wt.% VGCF were manually agitated together in a small quantity of acetone followed by evaporation of the acetone, which leaves the LCP pellets coated with VGCF. A series of LCP–VGCF mixtures was extruded in a single pass using a Brabender D-52 Intelli-Torque Plasti-corder with a D6/2 compounding twin-screw extruder–compounder (42 mm screw diameters; 7:1 L/D ratio). A horizontal stranding die was used with a cylindrical 1.59 mm diameter exit nozzle with an L/D ratio of 3:1. Temperature control was maintained in three independently controlled zones along the extruder and at the die. The first stage was set at 270 °C, the second stage at 280 °C, the third stage at 285 °C, and the extrusion die at 290 °C. The rotation speed of the extruder was initially set to 20–50 rpm during warm up with neat LCP and then to 25 rpm for extrusion. The average measured exit temperature of the LCP–VGCF extrudate was 322 °C. The extruded monofilament was collected just beyond the exit nozzle on a conveyor belt take-off with its speed manually adjusted to avoid kinking or necking of the extrudate. The diameter was reduced or enlarged, respectively, for conveyor take-up speeds greater or slower than the average extrusion speed at the die exit.

Tensile testing was performed to determine the modulus and ultimate strength as a function of VGCF concentration and monofilament extrusion diameter. Monofilament sections with ~100 mm gage-length were tested at room temperature at a constant cross-head speed of 1.3 mm min^{-1} (strain rate $\sim 2 \times 10^{-4}$ s^{-1}) using an Instron 4400R load frame. Monofilament diameters were determined by averaging four measurements taken along the gage-length. Specimens were held by wedge-compression grips fitted with grooved V-notch inserts. The small diameter and smooth surface of the filaments made the use of traditional extensometers problematic; therefore, engineering strain was calculated using the cross-head displacement. Witness marks were made on each specimen at both grips to detect gross slippage. A tangent modulus was determined using the maximum slope of a sliding series of linear least-squares fits to the stress–strain data. Each fit was applied to stress–strain points covering a 0.05% strain range that was incremented by one data-point for each fitting. A small amount of specimen slippage within the grips can be expected to have little effect on this initial modulus, since the slip would likely occur much later (i.e. at higher load). Tensile strength was calculated as the maximum load divided by the initial cross-section area.

Nanoindentation experiments were performed to determine the reduced modulus and hardness in the cross-section of a LCP–1% VGCF monofilament. The indenter used was a Hysitron Ubi 1™ with a diamond Berkovich tip (nominal radius 520 nm). The monofilament was cold-mounted and polished to a 0.05 μm finish. The load was programmed to increase linearly to 200 μN in 10 s, hold at the peak load for 5 s, and then unload linearly over 10 s. The indentations were spaced a minimum of 10 μm apart and the resulting data analyzed using the method of Oliver and Pharr [8].

Fracture surfaces of the monofilaments were coated with a thin layer of gold and examined under a field emission scanning electron microscope (LEO 1550) at an accelerating voltage of 5–15 kV.

Figure 1a is an SEM image of the as-received Pyrograf III VGCF showing extensive fiber clumping. In Figure 1b, individual fibers can be distinguished after being dispersed via ultrasonication in 1 wt.% sodium dodecyl sulfate (SDS) surfactant solution.

Figures 2 and 3 show the cross-section and surface of extruded LCP–VGCF monofilaments. The shade (light or dark) is indicative of VGCF content (low or high). The extruded cross-section (Fig. 2; 1% VGCF) shows higher concentrations of VGCF on the periphery than in the core region. Segregation of VGCF to the periph-

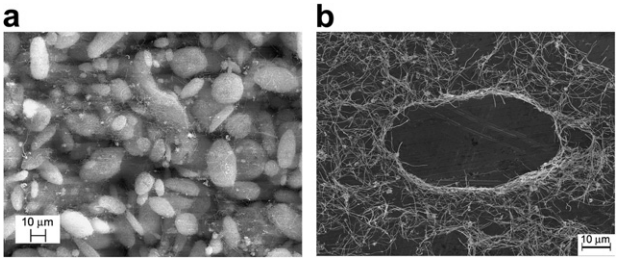

Figure 1. SEM images of the vapor-grown carbon fibers (VGCF): (a) in the as-received condition showing clumping; (b) VGCF after dispersion by ultrasonication in 1% SDS solution.

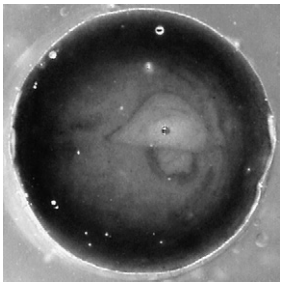

Figure 2. Optical microscope image of LCP–1% VGCF monofilament cross-section (diameter ~1.8 mm). The darker (lighter) shading at the circumference (core) indicates a higher (lower) VGCF concentration. The bright circumferential ring is a reflection from white light illumination.

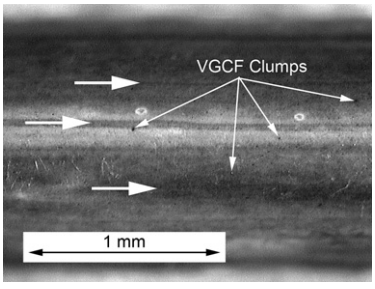

Figure 3. Optical microscope image of LCP–2% VGCF monofilament surface showing small black specks and banding, which indicate incomplete mixing and dispersion of the VGCF during extrusion.

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