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COMPRESSIVE STRENGTH OF AR MESOPHASE-DERIVED CARBON FIBERS: EFFECTS OF SPINNING DRAWDOWN RATIO

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Introduction

Mesophase pitch-based carbon fibers (MPCFs) are known for their lattice-related properties such as tensile modulus and thermal conductivity, which exceed 500 GPa and 200 W/m·K, respectively. However, MPCFs have inferior tensile and compressive strengths when compared to carbon fibers derived from polyacrylonitrile (PAN), with the latter exhibiting tensile strength over 6 GPa compared to 3 GPa for the former [1]. For this reason, PAN-based carbon fibers are preferred as reinforcement for applications in structural composites, hence making up to 90% of global carbon fiber market, while use of MPCFs as reinforcement is restricted to specialized applications in thermal management and aerospace. The improvement of the mechanical strength of MPCFs would help realize the potential of mesophase pitch as a high carbon yield precursor that can be obtained from inexpensive sources such as petroleum-refining residues [2].

To improve the mechanical strength of MPCFs, previous studies have found relationships between fiber processing conditions and carbon fiber tensile strength as a function of the transverse fiber microstructure. Mesophase pitch fibers are formed by melt spinning, which consists of the following steps: (i) melting of pitch, (ii) extrusion of molten pitch through spinneret capillaries, and (iii) draw-down of pitch filaments. Process conditions during melting and extrusion have been shown to influence the microstructure and properties of the resulting MPCFs. For example, lower spinning temperatures and no stirring before extrusion lead to radial transverse microstructure, which in turn leads to lower tensile strengths than those of non-radial microstructures [2]. Carbon fibers spun with stirring show non-radial microstructures, are less graphitizable, and have higher tensile strength [3].

During the draw-down step, for a constant spinneret capillary diameter, a higher winding speed leads to smaller as-spun diameters as a consequence of the conservation of mass. Smaller carbon fiber diameters are directly related to higher tensile strengths because of a smaller probability of occurrence of a critical defect in the smaller fiber surface/cross-section/volume. Therefore, higher take-up speeds have been indirectly linked to higher tensile strengths, because of the finer-diameter fibers thus produced. However, a higher take-up speed is not the only criterion for producing thinner fibers; capillary diameter is yet another factor as the use of a smaller capillary diameter can produce thinner fibers by using a smaller take-up speed. Thus, the drawdown ratio (DDR), which involves both the spinneret capillary diameter and the as-spun diameter, constitutes a more comprehensive variable to study the effects of spinning on the mechanical strength of MPCFs.

Also, because mesophase pitch consists of discotic molecules, in contrast to long-chain polymeric molecule for PAN, the effects of a more severe draw-down are not completely understood for pitch-based fiber processing. Therefore, the primary goal of this research is to investigate the effect of draw-down ratio (DDR) on mechanical properties of MPCFs, more specifically tensile and compressive strengths. The study was conducted for carbon fiber samples of equivalent fiber diameter and heat treatment conditions, to avoid confounding variables.

Materials and Methods

A synthetic, naphthalene-based AR pitch with 100% mesophase content and softening point of about 280°C (ASTM D3104) was used as precursor for the formation of pitch fibers. Melt spinning was carried out in a batch unit at a fixed spinning temperature of 305°C, using four custom-designed spinnerets, each one with the following capillary diameter, capillary length and number of holes: (i) 50 µm, 250 µm and 18 holes; (ii) 75 µm, 370 µm and 18 holes; (iii) 100 µm, 200 µm and 12 holes, and (iv) 150 µm, 300 µm and 12 holes.

Precursor pitch fibers were oxidatively stabilized over the temperature range 220-240°C to achieve a mass gain of 10-12%. Oxidized fibers were subsequently heat-treated in a high temperature furnace (Astro 1000, Thermal Technology LLC) to a final temperature of 2100°C. Tensile properties of carbon fibers were measured by single filament tensile testing (ASTM D3379-75) using a MTI Phoenix universal testing machine equipped with a 500 g load cell, using a crosshead velocity of 0.5 mm/min. Prior to tensile testing, fiber diameter of each specimen was measured by the laser diffraction technique. The load cell of the machine measured the force required to elongate the specimen, and the tensile stress was calculated as the force divided by fiber cross-section area. Values of tensile strength and tensile modulus were reported as average with a 95% level of confidence from a t-statistic.

The compressive strength of carbon fibers was determined by the single-filament tensile recoil test on the same testing machine used for tensile testing [4,5]. Filaments were pulled to a certain stress level and then split by a high-voltage electric arc causing the recoil of the two halves. The electric arc formed between two metal electrodes that had been brought within 5 mm of each side of the filament. The stress at which the filament had been subjected to right before the strike of the electric arc manifested into compressive stress upon recoil. Each half of the filament would either survive the recoil or fail under it, which was visually determined right after the arc strike. The analysis of the outcome of the tensile recoil test was assisted by a camera that recorded the strike of the electric arc splitting the filament.

Results and Discussion

Table 1 presents tensile strength of the experimental carbon fiber samples, along with their corresponding carbon fiber diameter (d_{cf}) and DDR. The samples have been grouped as pairs with similar fiber diameters (A1-A2, B1-B2, C1-C2, etc.) with group D having the smallest diameter

Table 1. Tensile properties and spinning conditions of experimental carbon fiber samples.

Sample	d_{cf}, µm	σ_t, GPa	DDR
A1	12-13	1.34 ± 0.24	117 ± 28
A2		1.92 ± 0.20	17 ± 3
B1	10-11	1.48 ± 0.26	58 ± 10
B2		1.84 ± 0.18	32 ± 3
C1	9-10	1.48 ± 0.30	44 ± 5
C2		2.16 ± 0.19	19 ± 3
D1	8-9.	1.42 ± 0.19	189 ± 29
D2		2.31 ± 0.28	14 ± 2

For all four pairs (having different diameters), the sample of low DDR has a higher tensile strength (statistical significant at $p = 0.05$). For instance, sample A2 produced at a lower DDR of 17 (vs 117 for A1) led to a higher tensile strength. This is in spite of the fact that sample B was produced from a smaller capillary diameter that led to a higher shear rate. Previous studies have reported that increased shear rate leads to reduced tensile properties in MPCFs [6]. Results presented in Table 1 indicate that a low DDR results in a significantly higher tensile strength for carbon fibers generated from similar spinning temperature, stabilization conditions and HTT, and with similar diameter, despite the expected detrimental effect of a greater $\gamma_{|app}$ on the tensile strength.

While specific DDR values have not been reported in literature studies, mechanical properties of carbon fiber samples were generally consistent with literature values for MPCFs [7]. Average carbon fiber diameter, tensile strength and tensile modulus are ~ 10 µm, 1.7 GPa and 480 GPa across samples heat-treated to 2100 °C.

Due to the more complex nature of the compressive test compared to that of the tensile test, tensile recoil tests were only performed on samples D1 and D2, in order to assess the differences in compressive strength between that pair of samples of contrasting drawdown ratios.

The tensile recoil was performed on samples D1 and D2 over a range of values of compressive stress upon recoil (σ_R) of about 600 to 1000 MPa. The analysis of the binary response data was divided in two bins of values of σ_R, ~ 600-800 MPa, and ~ 800-1000 MPa. In each case, the survival percentage was calculated for both top and bottom. Table 2 presents the survival percentages of each filament half for samples D1 and D2. The percentages were calculated on the basis of 20 specimens for each bin of σ_R values. For the range ~ 600-800 MPa of compressive stress, the average survival was 65% for sample D1 and 67% for sample D2. For the range ~ 800-1000 MPa of compressive stress, the average survival was only 35% for both samples. In other words, the percentage of filament half survival upon tensile recoil shows little difference between samples D1 and D2. This means that there are no significant differences in the compressive strength between the two carbon fiber samples of equivalent carbon fiber diameter and HTT, yet contrasting DDR. Overall, this means that lower DDR had a significant positive effect on tensile strength, without being detrimental for compressive strength.

Table 2. Survival percentage of each filament half upon tensile recoil testing.

Sample	600-800 MPa		800-100 MPa	
	Top	Bottom	Top	Bottom
D1	60	70	30	40
D2	70	65	35	35

Conclusions

Tensile and compressive properties of mesophase pitch-based carbon fibers of different spinning drawdown ratios yet equivalent fiber diameters and heat treatment were compared. The results of this study have revealed that a defect-limited property such as tensile strength is favored by a decreasing drawdown ratio. Thus, MPCF tensile strength was observed to increase from 1.42 ± 0.19 to 2.31 ± 0.28 GPa for a drop in DDR from 189 ± 29 to 14 ± 2, for constant fiber diameter about 8 µm and HTT of 2100 °C. This behavior represents an anomaly with respect to the typical one observed in PAN-based carbon fibers, for which an increased spinning DDR leads to improved mechanical strength, due to the enhanced molecular orientation along fiber axis. For MPCFs, an increased DDR can lead to more defects in the inter-crystalline regions leading to more significant weak links that decrease fiber strength. Also, the results of this study have revealed that compressive strength does not deteriorate due to the lower spinning drawdown.

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