Introduction

Over the last few decades, fiber-reinforced composite materials with superior mechanical properties have been developed for advanced aircraft, aerospace and sporting goods applications. In these performance-driven applications, carbon fibers have become the preferred reinforcement because of their superior mechanical and thermal properties as well as their chemical stability in inert environments [1-3]. Carbon fiber reinforced composites also offer weight savings compared with other traditional materials [4,5].

Nearly all carbon fibers are produced from one of the two precursors, mesophase pitch and polyacrylonitrile (PAN). PAN-base carbon fibers are preferred in applications where strength is critical whereas mesophase pitch-based carbon fibers are utilized in applications where stiffness or thermal conductivity is critical. Mesophase pitch-based fibers are melt spun from a liquid-crystalline, or mesophase, pitch precursor. The melt spinning process tends to orient the mesophase pitch molecules parallel to the fiber axis, and subsequent high temperature heat treatment enhances and perfects this orientation. In fact, mesophase pitch-based carbon fibers are commercially-available with tensile moduli approaching that of graphite (~1000 GPa). However, this graphitic structure makes mesophase pitch-based fibers more flaw-sensitive than PAN-based carbon fibers. As a result, the tensile strength of pitch-based carbon fibers tends to be lower than that of PAN-based carbon fibers [6].

Because of their remarkable electrical and tensile properties [7], many believe that carbon nanotubes could lead to an entirely new generation of fibers and composites with vastly increased properties [8]. Several researchers have tried to incorporate carbon nanotubes in polymeric matrices to produce composites with improved mechan-
Table 1. Reference Notation for Samples Tested in This Study

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Contents of MWNTs</th>
<th>Physical mixing</th>
<th>Chemical dispersion of MWNT</th>
<th>Reference name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor (pitch)</td>
<td>0.0 wt%</td>
<td>X</td>
<td>X</td>
<td>PM-MP</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td></td>
<td></td>
<td></td>
<td>PM-CF</td>
</tr>
<tr>
<td>Precursor (pitch)</td>
<td>0.0 wt%</td>
<td>O</td>
<td>X</td>
<td>UM-MP</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td></td>
<td></td>
<td></td>
<td>UM-CF</td>
</tr>
<tr>
<td>Precursor (pitch)</td>
<td>0.1 wt%</td>
<td>O</td>
<td>O</td>
<td>0.1 wt% MWNT-MP</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td></td>
<td></td>
<td></td>
<td>0.1 wt% MWNT-CF</td>
</tr>
<tr>
<td>Precursor (pitch)</td>
<td>0.3 wt%</td>
<td>O</td>
<td>O</td>
<td>0.3 wt% MWNT-MP</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td></td>
<td></td>
<td></td>
<td>0.3 wt% MWNT-CF</td>
</tr>
</tbody>
</table>

Physical and electrical properties [9-11]. However, the addition of small amounts of multi-wall nanotubes (MWNTs) might also enhance the properties of PAN- or pitch-based carbon fibers.

In this study, MWNTs were chemically modified to enhance dispersion and added to mesophase pitch precursors. Then the as-received mesophase pitch and the MWNT-containing pitch precursors were melt spun into fibers. The as-spun fibers were oxidized in air to render them infusible and carbonized at 1500 °C in an inert atmosphere. Scanning electron microscopy (SEM) was used to examine the microstructure of the carbon fibers. The mechanical properties were measured by using the Instron tensile tester. The morphology and mechanical properties of final fibers were investigated for three different batches of carbon fibers processed at the same conditions to verify that all results were consistent.

A four-point probe technique was used to measure the...
electrical resistivity the individual carbon fibers. The device consisted of a Teflon block with an open center and four brass posts located at each corner of the block. Four 80 µm diameter copper wire leads were connected to each post and extended across the center hole of the block, such that the wires were parallel. The four posts were attached to a Keithley Model 2000 A micro-ohmmeter, which supplied current to the outer wires and measured the resistance between the inner wires. Prior to testing, the length and area of each carbon fiber was measured. Then a single fiber was placed across four copper wires. A small amount of fast-drying silver conductive paint was applied to ensure contact between the wires and the fiber.

Results

Mesophase Pitch Containing MWNTs

Figure 1 shows the TEM images of as-supplied MWNTs and the chemically treated MWNTs. As Figure 1(a) shows, without any chemical treatment the MWNTs were highly agglomerated. After chemical treatment, the TEM images (Figure 1(b)) revealed that agglomeration decreased and the MWNTs were more evenly dispersed. This indicated that MWNTs would need to be chemically treated prior to being added to the mesophase pitch in order to ensure dispersion [16].

The softening points of various samples were measured to determine if the MWNTs would change the softening behavior of the mesophase pitch. The results are shown in Figure 2. The softening point of as-received mesophase pitch was about 274 °C, and the softening point increased as the quantity of MWNTs increased. Below 0.3 wt% MWNT-MP the increase in softening point was relatively small, but above this value the softening point increased more rapidly. Therefore, MWNT concentrations of 0.1 and 0.3 wt% MWNT in mesophase pitch were selected for further study.

Figure 3 shows the melt viscosities of a as-received mesophase pitch (PM-MP) and modified mesophase pitch (0.1 wt% MWNT-MP) as a function of shear rate. Both samples exhibit the region I and region II flow behavior typically observed for liquid crystalline polymers and mesophase pitches [17,18]. In region I, the viscosity decreases as the shear rate increases. In region II, which encompasses shear rates commonly encountered during fiber extrusion, the viscosity is almost constant. The results also indicated that the 0.1 wt% MWNT-MP was slightly more viscous than the PM-MP; however, the difference was not statistically significant. Consequently, the modified mesophase (0.1 wt% MWNT-MP) and the as-received mesophase pitch (PM-MP) were melt-spun at the same temperature.

Preparation of Mesophase Pitch-Based Carbon Fibers

The same batch spinning device was used to melt spin the as-received and modified mesophase pitches into fiber form. Initial experiments were conducted at a spinning temperature of 295 °C (approximately 20 °C above softening point of the mesophase). However, at this tem-
perature fiber breakage was frequent, even at the minimum take-up speed. The extrudate was apparently too viscous to drawdown so the spinning temperature was increased to 305 °C. At this temperature the spinnability was good, and very little fiber breakage was observed. The average diameters of as-spun PM-MP fibers were between 18 and 22 µm, depending on the exact winding speed. The spinnability of the 0.1 and 0.3 wt% MWNT-MP was not as good as that of the as-received mesophase. With both MWNT-containing mesophases, fiber breakage was frequent. This might be expected because the MWNTs appeared to form a solid suspension in the mesophase.

**Microstructure of Carbon Fibers**

The microstructure of these carbon fibers was studied because of its influence on mechanical properties such as the strength and modulus [16]. Figure 4 displays SEM micrographs of the carbonized fibers that were melt spun from the as-received and MWNT-containing mesophases. Carbonized fibers produced from the as-received mesophase (PM-CFs) exhibited a radial or open wedge (Pacman) structure (Figure 4(a)). The SEM micrographs would suggest that the graphene layers were radially-arranged across the transverse cross section of the fiber. Also, the micrographs suggest that the layers are aligned parallel to the fiber axis. This microstructure is often observed in high modulus fibers. Although not shown, carbonized fibers produced from the mixed as-received mesophase (UN-CF) also exhibited a radial structure. Figure 4(b) exhibits the SEM micrograph of 0.1 wt% MWNT-CFs. The fibers displayed a random structure within the plane although graphene layers still were aligned parallel to the fiber axis. Figure 4(c) shows a SEM micrograph of 0.3 wt% MWNT-CFs. Like the 0.1 wt% MWNT-CFs, the 0.3 wt% MWNT-CFs also displayed a random structure. Therefore, since the spinning and heat treatment conditions used to produce the as-received and MWNT-containing carbon fibers were similar, one can conclude that the MWNTs, rather than mixing, were responsible for changing the microstructure of the carbon fibers from radial to random.

**Figure 4.** SEM images of microstructure in (a) PM-CF, (b) 0.1 wt% MWNT-CF, and (c) 0.3 wt% MWNT-CF.

**Figure 5.** Evidence of MWNTs in 0.3 wt% MWNT-CF.

Mechanical Properties

The mechanical testing of PM-CFs, UM-CFs, and MWNT-CFs was performed on four replicate batches. An analysis of variance (ANOVA) was performed to verify the consistency between batches. The difference in the mechanical properties (tensile strength, modulus, and failure strains) of UM-CFs for each batch was statistically not
significant at 95% confidence interval. Similarly, the ANOVA analysis of PM-CFs showed that the difference was not significant. Therefore, these results indicate that the relative error between batches was negligible.

The tensile strength, modulus, and strain-to-failure of PM-CFs, UM-CFs, and MWNT-CFs are summarized in Figure 6. The tensile strength and modulus of UM-CFs were the highest among different samples. The tensile strength and modulus of PM-CFs were almost the same as those of UM-CFs. To compare the properties of UM-CFs and PM-CFs on a statistical basis, t-test was performed. There was no significant difference between UM-CFs and PM-CFs. Therefore, one can conclude that the mixing step did not influence the microstructure or mechanical properties of carbon fibers to any significant extent.

The results indicate that PM-CFs have a higher tensile strength and modulus than MWNT-CFs. The tensile strength of 0.1 wt% MWNT-CFs was about 1.3 GPa, whereas the tensile strength of PM-CFs was about 1.9 GPa. Also, the tensile strength of 0.3 wt% MWNT-CFs decreased to about half that of the 0.1 wt% MWNT-CFs. The modulus and strain-to-failure of MWNT-CFs were also lower than those of the PM-CFs and UM-CFs. Thus, as the amount of MWNTs in mesophase precursors increased, the mechanical properties of the carbon fibers decreased. This is also believed that the addition of the MWNTs in precursor make carbon fibers weaken due to change of micro structure from radial to random transverse textures within them. Mochida et al. have shown that fibers with random textures tend to exhibit lower tensile strength than those with radial structures [19]. Perhaps the interaction between graphene layers and MWNTs within the carbon fibers is not strong enough to improve the mechanical properties.

**Electric resistivity**

Figure 7 shows the electric resistivities of the carbon fibers. The electric resistivity of P-25, measured as a test-
Figure 8. SEM images of PM-CF and 0.1 wt% MWNT-CF in axial direction.

(a) PM-CF  (b) PM-CF at higher magnification

(c) 0.1 wt% MWNT-CF  (d) 0.1 wt% MWNT-CF at higher magnification

Figure 8. SEM images of PM-CF and 0.1 wt% MWNT-CF in axial direction.

The electrical resistivity of the UM-CFs was roughly 4 $\mu\Omega\cdot$m. This value was very close to the electric resistivity of the carbon fibers. Surprisingly, the electrical resistivity of the 0.1 wt% MWNT-CFs was approximately 25% lower than those of the carbon fibers that did not contain MWNTs. One might have expected the resistivities to be, at best, similar since, even though the addition of MWNTs changed the transverse texture from radial to random, the sheet-like graphene layer was still developed along fiber axis (Figure 8(b)). The 25% decrease is evidently the result of the well-oriented MWNTs parallel to the fiber axis. This argument is supported by Andrews and coworkers [20] who found that the single wall nanotubes reduced the electric resistivity of isotropic pitch-based carbon fibers.

**Conclusion**

From this study of mesophase pitch-based carbon fibers containing multi-wall nanotubes (MWNTs), the following conclusions can be drawn. Mesophase pitch containing up to 0.3 wt% MWNT-MP can be successfully spun into fibers at 305 $^\circ$C. The viscosity of the 0.1 wt% MWNT-MP was not significantly different than that of the as-received mesophase pitch. Microstructural analysis revealed that whereas the carbon fibers obtained from PM-MP had a radial transverse texture of graphene layers, the carbon fibers containing MWNTs had a random transverse texture. In previous literature studies, the microstructure of carbon fibers was changed by modifying the flow geometry of the precursor pitch. However, the microstructure of the carbon fibers in this study was modified by compositional change (the addition of MWNTs). Although the addition of MWNTs to the mesophase precursors did not increase the mechanical properties of the carbon fibers, the presence of the well-aligned MWNTs decreased the electric resistivity of the carbon fibers by about 25%.

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**References**


