HIGH THERMAL CONDUCTIVITY CARBON FIBERS FROM SUPERCRITICALLY EXTRACTED MESOPHASE PITCH

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Introduction

The production of less expensive carbon fibers with high moduli and high thermal conductivities will require a decrease in graphitization temperatures. This goal cannot be achieved without careful control of the as-spun, or green fiber structure and composition. Ideally, green fibers should be melt-spun from a precursor with no chemical impurities under conditions that will allow the development of a high degree of preferred orientation of the aromatic layers along the as-spun fiber axis.

In this paper, we report on our investigation of the melt spinning of ribbon-shaped fibers over a large range of spinning temperatures from four different mesophase pitches produced by supercritical extraction of an isotropic pitch. Wide-angle X-ray diffraction (WAXD) was used on as-spun fibers to evaluate their potential to yield final carbon fibers with the desired properties.

Experimental

Four mesophase pitch fractions, M1 through M4, were produced by supercritical toluene extraction of an isotropic pitch. A detailed description of the extraction apparatus and technique are available elsewhere [1, 2]. The molecular weight distributions of the fractions were obtained by gel permeation chromatography (GPC), and the chemical composition of the mesophases were studied by diffuse reflectance infrared spectroscopy (DRIFT). DRIFT was used to monitor the average size of the aromatic ring structures in the mesophases (referred to as the ortho-substitution index (OSI)), the extent to which these aromatic rings are substituted with alkyl groups (referred to as the C-H substitution index (CHSI)), and the extent to which the naphthenic molecules are substituted with alkyl groups (referred to as the alkyl index (AI)). The properties of the four mesophase pitches studied are shown in Table I.

The mesophases were melt-spun over a large spinning temperature range using a batch melt-spinning apparatus. This apparatus uses a positive-displacement gear pump, which fixes the extrusion flow rate. The mesophases were spun at a constant shear of 3930 ± 10 s^{-1} and at a constant drawdown ratio of 189 ± 2 to produce ribbon-shaped fibers with cross-sectional areas of about 350 μm^2.

The degree of misorientation of the aromatic layers with respect to the as-spun fiber axis (Z-values) were measured by WAXD using a Scintag XDS 2000 diffractometer.

Selected green fiber sets exhibiting high and low Z-values from each mesophase were stabilized at 250 °C for 2 h and graphitized at 2400 °C for 15 min. The tensile properties of the resulting carbon fibers were measured using an Instron Model TM, and the electrical resistivities were determined using a standard four-point probe technique. Electrical resistivity measurements were made to estimate the thermal conductivities of the fiber sets [3]. Finally, lattice parameter measurements were performed on the graphitized fibers using WAXD.

Results and Discussion

Figure 1 shows the influence of the spinning temperature on the Z-values of green fibers melt-spun from M1, M2, and M3. Generally, the misorientation of the molecules within the fibers decreased with increasing spinning temperature (up to a temperature at which the mesophase becomes too "watery"). The behavior observed is similar to that observed for round fibers spun from the same supercritically extracted mesophase [4]. Mesophase M4 could not be reproducibly melt-spun into the fiber form with the batch apparatus used due to off gassing. Incidentally, mesophase M4, in spite of high aromaticity, has the highest CHSI and AI of all mesophases studied. It can be speculated that the off gassing observed during the melt spinning of mesophase M4 originates from the large quantities of alkyls present on both aromatic rings and naphthenic groups.

For each spinnable mesophase, two sets of green ribbon-shaped fibers produced at low and high spinning temperatures, and hence, exhibiting high and low Z-values, respectively, were selected and processed into final carbon fibers. The fiber properties are shown in Table II.

For each mesophase studied, the Z-values of final carbon fibers correlated well with the corresponding as-

spun Z-values, i.e., a decrease in as-spun Z-values resulted, after heat treatment, in a decrease in Z-values within the final fibers. Similarly, the electrical resistivities decreased and the tensile moduli increased with decreasing as-spun Z-values. However, electrical resistivity is related to crystallite size as well as orientation, so the final fibers with the lowest electrical resistivities did not always exhibit the highest tensile moduli. The correlations between Z-values and electrical resistivities or tensile moduli were confirmed by the lattice parameters L_c and L_a, which showed an increase in the average crystallite size within the fibers with decreasing Z-values.

Unfortunately, Z-value comparisons between fiber sets spun from the different mesophases (which are chemically different) can not be made because the fibers in this study were heat-treated under the same conditions, not at their optimum.

Conclusions

The potential of ribbon-shaped fibers melt-spun from supercritically extracted mesophase to develop improved tensile moduli and thermal conductivities was studied. For carbon fibers spun from a given mesophase, the electrical resistivity decreased and tensile moduli increased with increasing spinning temperature or decreasing degree of misorientation of the aromatic layers within as-spun fibers.

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Table I. Properties of the Fiber Precursors.

Mesophase	M1	M2	M3	M4
Percent Mesophase (%)	90	100	100	100
Weight Average MW	1440	1550	1560	1580
Softening Point (°C)	238	265	274	300
C/H Ratio[a]	1.80	2.04	1.99	2.10
OSI[b]	0.276	0.266	0.253	0.259
CHSI[c]	0.473	0.474	0.466	0.498
AI[d]	0.405	0.425	0.427	0.458

[a] Atomic Ratio.
[b] An increase in OSI corresponds to smaller molecules.
[c] An increase in CHSI corresponds to larger amount of alkyl group.
[d] An increase in AI corresponds to larger amount of alkyl groups.

Table II. Properties of as-spun and final ribbon-shaped fibers spun from M1, M2, and M3.

Mesophase	M1		M2		M3	
T (°C)[a]	298	330	334	349	331	356
As-spun Z (°)	28.3	23.2	23.9	21.8	25.3	24.7
Final Z (°)	15.3	10.0	7.6	6.8	10.5	7.2
E (GPa)[b]	2.26	2.13	2.32	3.13	2.04	1.72
σ (GPa)[c]	439	698	422	493	820	846
ρ (μΩ.m)[d]	4.95	3.26	3.48	3.29	4.71	4.26
L_c (Å)[e]	133	193	134	110	172	203
L_a (Å)[f]	112	231	384	404	286	280

[a] Spinning Temperature
[b] Tensile Strength (±0.2)
[c] Tensile Modulus (±60)
[d] Electrical Resistivity (±0.2)
[e] Crytallite Stack Height
[f] Crystallite Coherence Length

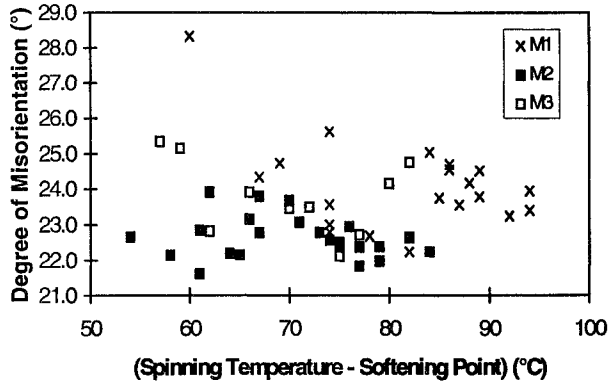

Figure 1. Z-values within ribbon fibers melt-spun from mesophases M1, M2, and M3.

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