Studies on “Mesophase”-Pitch-Based Carbon Fibers: Part II
Mechanical Properties and Thermal Expansion

Yasuhiro TANABE*, Eiichi YASUDA*, Katsuhiro YAMAGUCHI**,
Michio INAGAKI*** and Yasuhiro YAMADA****

(Received 2 October, 1990)

*, **RLEM, Tokyo Institute of Technology
Nagatsuta, Midori, Yokohama 227, JAPAN
***Toyohashi University of Technology
Tenpaku, Toyohashi 440, JAPAN
****Government Industrial Research Institute, Kyushu
Tosu, Saga 841, JAPAN

Mechanical properties such as strength, modulus and strain to break, and coefficients of thermal expansion of mesophase-pitch-based carbon fibers were measured using the fibers with four different microtextures heat-treated at two different temperatures. The textures were radial with wedge, radial, random and onion. In strain to break of the fibers, there were not so much difference with different microtextures. Young's moduli, however, were different with microtextures, especially in graphitized fibers. The modulus correspond to the orientation function, and to crystallographical parameters. The fiber with higher modulus seemed to be stronger. Coefficients of thermal expansion of the carbonized fibers were able to be classified into two groups; those of the fibers with radial with wedge/random and with radial/onion, but those of graphitized ones were in the same level. The coefficients were smaller than those of PAN-based fibers with the same Young's moduli.

KEYWORDS: Mechanical properties, Thermal expansion, Microtexture, Mesophase-pitch-based carbon fiber, Orientation function

1. INTRODUCTION

Recently, many types of pitch-based carbon fibers (CFs) have been developed and those derived from mesophase pitches (mesophase-pitch-based carbon fibers) are particularly attracting the attention from different points of view. Now some of them are available in commercial market. General properties of mesophase-pitch-based CFs and the microtextures have been compiled in the references No. 1 and 2. Microtextures of these fibers can be roughly classified into three categories; radial, random and onion3).

The CF with radial-type microtexture is inclined to have a wedge-opening and the strength tend to be lower than those with other textures3). However, the wedge-opening is not a serious defect for weakening the carbon fibers, because the opening is extended along the fiber axis. Crystallites orientation in CFs may play an important role to dominate the mechanical properties of fibers. Papers reported the relation between microtextures and pro-
Properties are few. Only one paper deals with the relation between mechanical properties and thermal properties.

In this paper, mechanical properties and thermal expansion of mesophase-pitch-based carbon fibers with different microtextures are studied and discussed in the relation to the crystallographical geometry (orientation) and the parameters in CFs. Eight types of CFs, produced from the same raw material pitch, were used in the experiment.

2. EXPERIMENTAL PROCEDURES

2.1 Carbon Fibers

The CFs, having four different types of microtextures in their cross-sections, were prepared from the same coal-tar pitch with a method in the laboratory of one of the authors (Y.Y in GIRI Kyushu). The CFs were heat-treated at 1200°C (carbonized) and then up to 2600–2800°C (graphitized). In Table 1, the microtextures in cross-sections and averaged diameters are summarized. The detailed structures and microtextures of the CFs used were reported as the part. X-ray parameters of crystallites and anisotropy ratios determined from magneto-resistance of the graphitized CFs are compiled in the same Table.

The PAN-based carbon fibers (T-300, M-40 and T-800: Toray Ltd.) were also used as references materials.

2.2 Mechanical Properties

Strength, Young's modulus and strain to break were measured at room temperature (RT)

Table 1 Textures and diameters of the carbon fibers used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat-treatment °C, min</th>
<th>Texture</th>
<th>Diameter μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-1</td>
<td>carbonized 1200, 60; graphitized 2800, 60</td>
<td>radial with wedge</td>
<td>17.1, 14.1</td>
</tr>
<tr>
<td>I-2</td>
<td>carbonized 1200, 60; graphitized 2800, 60</td>
<td>radial</td>
<td>13.7, 13.0</td>
</tr>
<tr>
<td>I-3</td>
<td>carbonized 1200, 60; graphitized 2600, 60</td>
<td>random</td>
<td>10.5, 10.2</td>
</tr>
<tr>
<td>I-4</td>
<td>carbonized 1200, 60; graphitized 2600, 60</td>
<td>onion</td>
<td>9.0, 9.1</td>
</tr>
</tbody>
</table>

Table 2 X-ray parameters and magnetoresistance date of the graphitized carbon fibers. [Ref. No. 6]

<table>
<thead>
<tr>
<th>Sample</th>
<th>c₀</th>
<th>Lc(004)</th>
<th>a₀</th>
<th>La(110)</th>
<th>rₜ</th>
<th>rTL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-1</td>
<td>6.741</td>
<td>180</td>
<td>2.460</td>
<td>640</td>
<td>0.670</td>
<td>0.0163</td>
</tr>
<tr>
<td>I-2</td>
<td>6.802</td>
<td>90</td>
<td>2.455</td>
<td>200</td>
<td>0.848</td>
<td>0.030</td>
</tr>
<tr>
<td>I-3</td>
<td>6.789</td>
<td>100</td>
<td>2.457</td>
<td>230</td>
<td>0.922</td>
<td>0.064</td>
</tr>
<tr>
<td>I-4</td>
<td>6.783</td>
<td>100</td>
<td>2.459</td>
<td>290</td>
<td>0.893</td>
<td>0.037</td>
</tr>
</tbody>
</table>
using mono-filaments according to the procedure in the Japanese Industrial Standard (JIS R-7601). A filament was cemented onto a carton with the gauge length of 25 mm. The carton was mounted on an Instron-type testing machine, and then cut at the center of the carton. The filament was tensioned with the speed of 0.5 mm/min. Forty filaments in each CF sample were tested. The Young's modulus of the CFs was calculated from the stress-strain diagram.

The cross sectional areas of all the fibers tested were measured on the fractured surfaces by a scanning electron microscope (SEM).

2.3 Thermal Expansion

Thermal expansion of the CFs from RT to 1000 °C were measured. Filaments (about 500 filaments) were cemented to small blocks made of a C/C composite in both ends. The blocks were clipped to an equipment. The fiber length was 50.0 mm. The expansion data were stored into a microcomputer. The detailed procedure was reported elsewhere.

The experimental error in coefficients of thermal expansion (CTE) was in a range of 0.06 x 10^-6 K^-1.

2.4 Orientation Function of Crystallites

Orientation functions of graphite layers in the CFs were determined from the X-ray diffraction intensity as a function of rotation angles at the position of (002) diffraction. The full width at the half maximum (Orientation Angle; OA) of the function was calculated from the profile. Curve fitting for the function was carried out in a form of \( \sin^m \theta \). The m value represents the function.

3. RESULTS

3.1 Mechanical Properties

Strength, Young's modulus and strain to break of the CFs are shown in Figs. 1, 2 and 3, respectively. The open marks indicate the values for the carbonized CFs and the closed indicate those for the graphitized ones. The values of T-300 and M-40 are also shown with the open and closed marks, respectively. Each mark stands for the averaged value of respective property and the bar for the standard deviation of experimental values.

---

Fig. 1 Strengths of the carbon fibers.

Fig. 2 Young's moduli of the carbon fibers.

Fig. 3 Strains to break of the carbon fibers.
The strength values of the carbonized I-2, I-3 and I-4 (according to the codes in Part I: I-2-12, I-3-12 and I-4-12) are about 1.7 GPa, and those of the graphitized ones around 1.6 – 1.8 GPa (Fig. 1). The carbonized I-1 (I-1-12) is weaker than other three, but graphitized one is stronger.

Influence of the diameters to the strength of CFs is not observed in every CF sample.

Young’s moduli of all carbonized CFs are around 140 GPa. In graphitized CFs, however, Young’s moduli are different with different textures. I-1 (I-1-28) has the highest and I-2 (I-2-26) the lowest.

Strain to break of all the carbonized CFs except I-1 (I-1-12) are about 1.3%, and that of I-1 (I-1-12) is about 0.6%. All graphitized CFs are broken at about 0.5% in strain (Fig. 3).

3.2 Thermal Expansion

The CTEs of the carbonized and graphitized CFs are shown in Fig. 4, respectively. All the carbonized CFs have larger CTEs than that of M-40 at whole range of measurement temperature (Fig. 4). I-2 and I-4 (I-2-12 and I-4-12) expanding more than I-1 and I-3 (I-1-12 and I-3-12). In graphitized CFs (Fig. 4), however, the CTEs are nearly the same and appreciably smaller than that of M-40.

3.3 Orientation Function

The values of OA and of m for the CFs are compiled in Table 3. In the carbonized CFs, the angles become large in the order of I-2,
I-1, I-4 and I-3 (I-2-12, I-1-12, I-4-12 and I-3-12). In the graphitized ones, they are in the order of I-1, I-2, I-4 and I-3 (I-1-28, I-2-28, I-4-26 and I-3-26).

4. DISCUSSION

The orientation angle, OA, was large and the m value was small in all of the carbonized CFs, suggesting that preferred orientation of carbon layers along the fiber axis was not remarkable in carbonized CFs. In the graphitized CFs, on the other hand, rather high degree of orientation was observed, especially in the sample I-1 (I-1-28). The OA angle of the graphitized CFs measured by X-ray corresponded well to the anisotropy ratio rTL determined by magneto-resistance data, which was a measure of the crystallite orientation along the fiber axis (see Table 2).

The order in the strength of the CFs corresponded to that in their Young's modulus; the higher the Young's modulus the stronger the CF, both in the carbonized and the graphitized CFs. The Young's moduli had direct relation to the a0 and/or the L3 (in Table 2), at least for the graphitized ones. Therefore, the strength also corresponded to these parameters.

Young's modulus of carbonized I-1 (I-1-12) was not so low, therefore I-1 must be stronger among the carbonized CFs. However, I-1 (I-1-12) showed low strength as compared with the others. The reason might be related to the existence of scale-like defects (upper in Fig. 5) or oblique layered defects (lower in Fig. 5) in the periphery of wedge-opening. Stress was concentrated at the defects and the defects might act as a failure origin. They disappeared and the periphery of the opening became flat, according to the crystallization in the CF by heat-treatment at high temperature. The disappearance and the increase in strength of the graphitized I-1 (I-1-28) are evidence for supporting this explanation.

Young's modulus of the CFs was calculated numerically using a simple approach as follows; CF consists of a series of crystallites which differed in an orientation with respect to the fiber axis. The compliance \( C(\theta) \) of a crystallite at angle \( \theta \) to the axis is expressed in equation (1).

\[
\begin{align*}
C(\theta) &= S_{11} \sin^4 \theta + S_{33} \cos^4 \theta \\
&\quad + (2 \times S_{13} + S_{44}) \sin^2 \theta \cos^2 \theta 
\end{align*}
\]

(1)

\( S_{11} = 0.98 \times 10^{-3} \text{ GPa}^{-1} \)

\( S_{33} = 27.5 \times 10^{-3} \text{ GPa}^{-1} \)

\( S_{13} = -0.33 \times 10^{-3} \text{ GPa}^{-1} \)

\( S_{44} = 240 \times 10^{-3} \text{ GPa}^{-1} \)

It is reasonably assumed that the compliance of a CF is simply described by the summation of the products of the crystallite compliance and the orientation function. Therefore, the calculated modulus \( E_{\text{calc}} \) of the CF is given by the following equation;

\[
E_{\text{calc}} = \left( \frac{1}{\pi} \int_0^{\pi} \frac{C(\theta) \sin^2 \theta d\theta}{\sin^2 \theta d\theta} \right)^{-1}
\]

(2)

In Fig. 6, the measured moduli are plotted against the calculated moduli. The calculated modulus described well the measured modulus not only on the mesophase-pitch-based but also PAN-based CFs. This result indicates that the modulus of both PAN and pitch-based CFs can be explained by the equation (2).

The above discussion suggested that the crystallographical orientation parameters play
Mechanical Properties and Thermal Expansion

Fig. 6 Measured and calculated Young's moduli of the carbon fibers.
open marks: carbonized
closed marks: graphitized

Fig. 7 Coefficients of thermal expansion (CTEs) of the carbon fibers at room temperature as a function of the orientation angles (OA).
open marks: carbonized
closed marks: graphitized

an important role to dominate the modulus, therefore, the strength in the mesophase-pitch-based carbon fibers. In PAN-based fibers, the strength of the fibers which contain high concentration of misorientation is usually higher than that of the fibers with highly oriented texture; e.g. T-type fibers having higher strength than the M-type fibers made by Toray Ltd. This relation between Young's modulus and tensile strength for the PAN-based CFs seems to be opposite to that of the mesophase-pitch-based CFs founded in this work. This might be explained as follows; in fibers with small basal planes (small crystallites) as PAN-based fibers, it is difficult to stress the planes uniformly, in other words, stress concentrate at the boundary of the crystallites. In this case, a structure consists of crystallites plays an important role to dominate the strength of the CF. A folded structure, which can expand, is suitable for being stressed uniformly as compared with flat one. Therefore the crystallographical parameters dose not correspond directly to the strength in PAN-based fibers. On the other hand, in carbon fibers with large basal planes as in mesophase-pitch-based carbon fibers\(^9\), the structure is comparatively flat and stress can be induced uniformly to the basal planes, and then the fiber has a possibility to be strong. In this case, the strength and Young's modulus of the fibers increase with growth of the basal plane of graphite.

In Fig. 7, the relation between CTE at room temperature vs. orientation angle is shown. A general trend was that the fibers with larger OA-value, in other words, with poor orientation had larger CTE. However, the relation in the PAN-based CFs was a little bit different from that in the mesophase-pitch-based ones. The CTEs of the mesophase-pitch-based CFs were smaller than those of the PAN-based ones for the same OA. The reason seem to be one of the following possibilities; (1) crystallites of mesophase-pitch-based CFs are larger than those of PAN-based\(^10\), (2) effect of void on thermal expansion is different between the two fibers\(^11\), (3) orientation direction of graphite hexagonal rings is different in pitch-based and in PAN-based fibers, as reported by Plaetschke and Ruland\(^12\).

CTEs of the CFs have also been discussed on the basis of the orientation function and the CTE of the graphite crystallite\(^13\). The same approach as done in the modulus was carried out to estimate the CTE from the equation (3).

\[
\text{CTE}_{\text{calc}} = \frac{\left(\alpha_t \cos^2 \theta + \alpha_p \sin^2 \theta\right) \sin^m \theta}{\int \sin^m \theta \, d\theta} \quad \text{(3)}
\]
here, $\alpha_t$: CTE of the crystallite in the direction of c-axis
$\alpha_p$: CTE of the crystallite in the direction of a-axis

When $\alpha_p$ and $\alpha_t$ were assumed as the values of a single crystal such as $\alpha_p = 1.8 \times 10^{-6}$ K$^{-1}$, $\alpha_t = 27 \times 10^{-6}$ K$^{-1}$, the calculated CTE could not agree with the measured CTE; the calculated CTEs being much higher than those of the measured ones. This suggested that the expansion of a crystallite in the direction of c-axis was restricted by a-axis expansion of surrounding crystallites. Best fitting of the calculated CTE to the measured one for all the CFs was realized, when $\alpha_t$ was $13 \times 10^{-6}$ K$^{-1}$. The relation is shown in Fig. 8. The value of CTE was about the half of the single crystal value.

$\alpha_t$ was estimated in each CF for the best fitting of the CTE$_{calc}$ to the measured CTE in the case of $\alpha_p = -1.8 \times 10^{-6}$ K$^{-1}$. The estimated $\alpha_t$s are plotted as a function of m values in Fig. 9. In the mesophase-pitch-based CFs, crystallites expansion in c-axis was restricted as compared with the PAN-based carbon fibers. The relations between $\alpha_t$ and m were classified into three; I-1/I-2, I-3/I-4 and PAN-based ones. This might be caused from microtexture difference in the CFs.

Young's modulus is plotted as a function of CTE in Fig. 10; the larger CTE corresponds to the smaller modulus. As is easily understood from Fig. 6, 7 and 8, the relation is a little bit
different in between pitch-based and PAN-based CFs. The CTEs of the PAN-based CFs seemed to be higher than those of the mesophase-pitch-based CFs with the same Young’s modulus. This characterizes the mesophase-pitch-based CFs from the PAN-based ones, which is supposed to come from the difference in the relation between the orientation angle and the CTE.

5. CONCLUSION

Mechanical properties and thermal expansion coefficients were measured on eight types of the mesophase-pitch-based carbon fibers made from the same raw pitch. The followings were concluded;

(1) Microtexture did not affect on Young’s modulus of carbonized CFs but did on that of graphitized CFs.
(2) Heat-treatment temperature affected on the strain to break, but microtexture not on it.
(3) The change in mechanical properties of I-1 (radial with wedge) with high temperature heat-treatment was much different from those of others. It might be caused from its high degree of orientation.
(4) Young’s modulus of the CFs could be estimated by a simple model by taking account of the orientation function of the crystallites.
(5) Pitch-based fibers had lower CTE than PAN-based ones with the same Young’s modulus.

ACKNOWLEDGEMENT

This study was partially supported by Monbusho International Scientific Research Program – Joint Research (No. 63044067) for 1988 and 1989.

The authors wish to thank Prof. Hirayama of Tokai University for his help.

REFERENCES