General paper

Effect of Cross-Sectional Textures on Transverse Compressive Properties of Pitch-Based Carbon Fibers

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Abstract: The effect of the orientation texture of cross-sectional graphitic layer planes on transverse compressive properties was studied in pitch-based carbon fibers. The finite element analysis indicated that radially oriented fiber could be expected to display higher transverse modulus and lower transverse compressive strength than randomly oriented fiber. The transverse compressive test was carried out by means of direct pressing of single filaments in which each filament's strength and modulus were measured. The cross-sectional orientation texture was identified not only by observation under scanning electron microscope (SEM) but also by torsional modulus measurement. The transverse modulus and transverse compressive strength were found to decrease with increasing crystallite size. It was however not possible to find out clear differences between radially and randomly oriented fiber. These transverse properties cannot therefore be attributed to differences in cross-sectional texture. Bonding between crystallites appears to be the dominant factor in determining the transverse modulus, while the strength in the central area of the cross section is expected to determine the transverse compressive strength of the filament.

Key Words: Transverse compressive properties, Carbon fiber, Orientation texture, Torsional modulus, Fractography

1. INTRODUCTION

Carbon fibers have high longitudinal modulus and tensile strength and are utilized for reinforcement of composite materials. One of the important advantages of composite materials is that they can create desirable specifications. Accurate design requires mechanical properties in all directions of reinforcement. As the texture of carbon fiber is anisotropic, its mechanical properties are also extremely anisotropic. However, the data commonly available to the designer cover only longitudinal tensile properties. Although the longitudinal compressive properties have reportedly been measured using recoil method [1, 2], elastica loop method [3] and other more direct methods [4-6], data from different methods show poor correspondence. As for transverse compressive properties, while there have been some reports on direct compressive test of single filament [7-11], few reports have addressed the relation between transverse properties and the texture or structure of fiber, an area of investigation nevertheless which might be important for the development of fibers of higher performance [8].

The authors have undertaken direct transverse compressive test of single carbon filament [7, 8] as a means to understand the relationship between texture or structure and transverse properties better. It has been reported that the transverse compressive strength of PAN-based carbon fibers is 3 to 5 times greater than that of pitch-based carbon fibers. The difference was attributed to textural differences in cross-sectional graphitic layer planes. In the present paper, the results of direct transverse compressive tests of pitch-based carbon filaments with different cross-sectional textures are presented. Analytical results based on the finite element method (FEM) are also given. In addition to scanning electron microscope (SEM) observation of a trans-

versely fractured filament, single filament torsional test was also carried out. The main factors determining transverse compressive properties are discussed in light of the results.

2. EXPERIMENTAL

The fibers used were pitch-based carbon fibers with randomly and radially oriented textures in the cross-sectional graphitic layer planes (hereinafter, random fiber and radial fiber). Both fibers were prepared from the same mesophase pitch precursor. Fibers with several different crystallite dimensions in the c-direction were prepared by varying heat treatment temperature from 1000 to 3020°C.

Diameter of each fiber, whose cross section was almost a circle, was measured by laser diffraction. The crystallite dimension in the c-direction, L_c , was determined from the X-ray diffraction pattern of the powdered fiber by evaluating the peak width at half-maximum peak height of the (002) lines using the Sherrer formula. Single filament tensile test was carried out according to JIS R7601 to obtain longitudinal modulus and tensile strength. More than 60 filaments were tested for each fiber. In Table 1, each fiber's longitudinal modulus, tensile strength, diameter and L_c are listed.

The equipment used for the transverse compressive test of single carbon filament was based on a microhardness tester [7]. It had a punch with a 36.8 μm square diamond face, which was flat, and not sharp like that of a hardness tester. Filaments were placed parallel to one side of the punch on a hard steel base and pressed with the punch. The compressed length of filament was thus 36.8 μm . Three filaments of each kind of fiber were tested. System compliance was evaluated from the difference between force-displacement diagrams for one-filament compression and two-filament compression. These three filaments were cut from

a single filament of about 5 centimeters in length.

Transverse modulus, E_T , was calculated from the slope of a measured force-displacement diagram, applying an equation for isotropic material in the cross section [9]. Transverse compressive strength, σ_T , was defined as the compressive stress exerted on the central area of the cross section in the loading direction at the moment of fracture. If isotropic material in the cross section is assumed, this σ_T is

expressed by

$$\sigma_T = \alpha \cdot \left[1 - \left(\frac{b_c}{r} \right)^2 \right] \cdot \frac{F_T}{\pi \cdot r \cdot t}, \quad (1)$$

where F_T is compressive force at moment of fracture, b_c is half of contact width at moment of fracture, r is fiber radius, t is length of contact with punch (36.8 μm), and α is stress concentration factor as a function of b_c/r [12].

After the transverse compressive test, the fractured sample on the base was subjected to SEM as it was and observed from the loading direction. The compression behavior of virgin fibers was also observed under SEM from the fiber axial direction. Several tens of filaments were placed between two stainless steel plates with sharpened edges. The end of the filaments were aligned with the edges of the plates by breaking off any protruding length. The stainless steel plates were compressed using a tension-compression device and the filaments were observed under SEM.

FEM analysis was carried out to evaluate the stress distribution in the cross section during transverse compression, using ANSYS Revision 5.0 from Swanson Analysis Systems, Inc. Torsional modulus was determined by torsional pendulum test of single filament [13].

3. RESULTS

3.1. FEM Analysis

FEM analysis was carried out assuming the cross section to be a circle. Divisions into elements are shown in Fig. 1. The modulus of the graphite crystal in the a-direction is about 29 times higher than in the c-direction [14]. In radially oriented texture, the a-axes of the graphite crystal-lites are arranged preferentially along the radius. No preferential orientation was expected in randomly oriented tex-

Table 1. Properties of pitch-based fibers.

Fiber	Diameter (mm)	σ_L (GPa)	E_L (GPa)	L_c (nm)
Random -A	10.13	2.51	132	1.1
Random -B	9.91	2.71	166	1.9
Random -C	9.42	3.42	240	4.9
Random -D	9.18	3.49	411	10
Random -E	9.24	3.66	480	15
Random -F	9.22	3.55	543	18
Random -G	9.22	3.68	576	19
Random -H	9.26	3.68	622	24
Radial -A	10.24	1.53	100	1.1
Radial -B	10.11	2.40	119	1.8
Radial -C	9.66	2.51	155	4.1
Radial -D	9.36	2.55	226	8.7
Radial -E	9.12	2.83	281	12
Radial -F	9.34	2.99	317	15
Radial -G	9.40	3.01	364	17
Radial -H	9.32	2.87	409	20

σ_L and E_L are longitudinal tensile strength and modulus, respectively.

Fig. 1. Stress distribution of σ_{yy} (y axis is loading direction) in the cross section when a fiber is compressed by 8% of its diameter by FEM. (a) simulation of random orientation texture and (b) simulation of radial orientation texture. Division into elements is also shown. Dimension is normalized by that before compression. Stress level is also normalized by that corresponding to 0.06 strain of random fiber constituent.

Fig. 2. Typical examples of force-displacement diagrams for 4 fibers.

ture. In order to simulate such textures in the cross section, the modulus along the radius and along the circumference was varied. That is, the modulus along the radius and along the circumference was made equal for random fiber which was thus considered quasi-isotropic. While radial fiber was simulated by setting a higher modulus along the radius. From the preferred orientation of graphitic layer planes along fiber axis for similar fibers, the ratio between the modulus along the radius and along the circumference for radial fiber was estimated at 4 : 1 to 9 : 1. In this analysis, it was set at 5 : 1; for random fiber, the modulus was set at 5/3 relative to radial fiber. That is, a ratio of 15 : 3 : 5 was used for the modulus along the radius for radial fiber, the modulus along the circumference for radial fiber and the modulus for random fiber. The Poisson's ratio was set at 0.3 [15] and shear modulus in the non-layers' direction was set at the same value of 0.64 in both fibers for comparison.

Load boundary condition was applied by the displacement of the rigid body by 8% of the fiber radius in the one fourth model as shown in Fig. 1. The rigid body was connected to the fiber parts with contact elements. The stress distribution along the y -direction (σ_y) on these conditions is shown in Fig. 1. It can be seen that the stresses are more concentrated beneath the load-bearing section in the radial fiber (b) than in the random fiber (a). Especially at the center, stress concentration is very high in radial fiber. The stress in the y -direction at the center of the radial fiber is about 8 times that in the random fiber. FEM analysis also showed that transverse modulus in radial fiber is 1.5 times that in random fiber. These results suggest that radial fibers possesses higher transverse modulus and lower transverse compressive strength.

3.2. Transverse Modulus and Transverse Compressive Strength

Typical examples of force-displacement diagrams are shown in Fig. 2. Lowly graphitized fibers showed rather linear relation. On the other hand, highly graphitized fibers

Fig. 3. The transverse modulus variation according to crystallite dimension, L_c , for random and radial fibers. Data of PAN-based fibers are also plotted for comparison.

Fig. 4. The transverse compressive strength variation according to crystallite dimension, L_c , for random and radial fibers. Data of PAN-based fibers are also plotted for comparison.

were showing nonlinearity, as previously reported [7, 9]. The transverse modulus and transverse compressive strength were evaluated from force-displacement diagrams as described in chapter 2.

Figure 3 shows the relation between the transverse modulus and L_c . Data from PAN-based fibers [7] are also plotted for comparison. The transverse modulus decreases with increasing L_c . Pitch-based fibers show similar moduli to PAN-based fibers. However, the clear difference between random and radial fibers, which had been expected from the results of the FEM analysis described above, was not observed.

Figure 4 shows the variation in the transverse compressive

Fig. 5. Appearance of fragments of transversely compressed radial fibers; (a) fiber with L_c of 1.8 nm and (b) fiber with L_c of 15 nm.

Fig. 6. SEM photographs of fractured fibers observed from fiber axial direction; (a) random fiber with L_c of 18 nm, and (b) radial fiber with L_c of 15 nm. Arrows show loading direction.

sive strength according to L_c . Results for PAN-based fibers [7] are also plotted. The transverse compressive strength decreases with increasing L_c for both pitch- and PAN-based fibers though pitch-based fibers show much lower strength for the same L_c . This is a different feature from that in the transverse modulus. However, no difference between random and radial fibers was seen in the strength, just like in the transverse modulus.

3.3. SEM Observation

Figure 5 shows the effect of crystallite size on the behavior of transversely compressed and fractured radial fibers. The fractured section is much longer than the length in contact with the diamond punch (36.8 μm). Fibers with less crystallite were broken into many smaller pieces, whereas the fragments of fibers with more crystallite were fewer and larger. Random fibers showed the same behav-

ior. This link between crystallite size and fragment size was also observed in PAN-based fibers [7], although the size and aspect ratio of the fragments was smaller than those in pitch-based fibers, and the length of the fractured section was limited.

Figure 6 shows the fractured fibers viewed from the fiber axial direction. The fibers shown are a random fiber with L_c of 18 nm and a radial fiber with L_c of 15 nm, and are both well-graphitized. The arrows show the compressive loading direction. The observed fracture paths formed almost straight lines running through the center of the cross section and the edge of the contact area.

4. DISCUSSION

4.1. Micro Textures

Randomly oriented and radially oriented textures were

Fig. 7. Torsional modulus according to crystallite dimension, L_c .

identified from a transverse cross section observed under SEM as shown in Fig. 6. The results of FEM analysis indicate that radial fibers could be expected to show higher transverse modulus and lower transverse compressive strength than random fibers. However, as shown in Figs. 3 and 4, no clear difference in the transverse modulus and transverse compressive strength was found between the two types of fiber. In order to confirm the difference in cross-sectional micro texture, torsional moduli were measured, as torsional modulus of carbon fiber is reported to depend on the preferred orientation of cross-sectional graphitic layer planes [13]. Figure 7 is the plot of torsional modulus against L_c . A clear difference between random and radial fibers is observed, with the former showing one and a half to two times higher torsional modulus at the same L_c . These values are comparable with torsional moduli of other pitch-based fibers [13]. The transverse modulus and transverse compressive strength may thus be mainly determined by factors other than cross-sectional texture.

4.2. Transverse Modulus

The findings shown in Fig. 7 confirm the difference in cross-sectional micro texture between random and radial fibers. However, as shown in Fig. 3, no difference between random and radial fibers was detected in the transverse modulus variation. In addition, graphitization process does not cause the change of cross-sectional orientation texture though it causes the increase of L_c . Therefore, the transverse modulus will not vary with graphitization if orientation texture is the dominant factor in deciding it. As seen in Fig. 3, however, the transverse modulus decreased from 18 to 3 GPa with increasing L_c in both random and radial fibers. Cross-sectional orientation texture therefore cannot be the main factor in deciding the transverse modulus.

As mentioned in 3.2., highly graphitized fibers show a nonlinearity in force-displacement diagrams. That is, force

Fig. 8. Illustration showing model for buckling of array of crystallites in the cross section, which causes nonlinearity in force-displacement diagrams. First, (A) crystallites shrink with load. Next, (B) they buckle with higher load. (C) is recovery period.

increases linearly with increasing displacement until unspecified displacement, but afterwards the rate of increase decreases gradually. In cyclic loading, loading and unloading processes do not follow the same path in force-displacement diagrams [7, 9]. The slope of force-displacement diagrams in the initial stage does not change between first and second loadings [7, 9].

Kawabata has suggested "slippage between crystallites" to explain some of these phenomena [9]. The mechanism of this model assumes the direction of friction among crystallites to be opposite between during loading and unloading. His mechanism, however, cannot explain the nonlinearity of the force-displacement diagram mentioned above. A buckling model of crystallite array is therefore proposed as shown in Fig. 8. When the array of crystallites is compressed, the initial shrinkage is schematically indicated as stage (A) in Fig. 8. This process is considered to correspond to the initial linear relation in the force-displacement diagrams. If deformation is large and binding with surrounding crystallites is not strong, it will buckle (B) on the way of loading. This is considered to be the nonlinear relation obtained for highly graphitized fibers. During the unloading cycle, not the reverse (A) stage but (C) stage will occur.

When graphitization is not sufficient, many amorphous parts which connect crystallites remain. With the progress of graphitization, neighboring crystallites combine into larger masses and amorphous parts decrease. The coalescence of crystallites leads to weakening of the bonds between them. Rigidity between crystallites thus decreases with the progress of graphitization. When graphitization has progressed sufficiently, weakened bonding between crys-

tallites produces nonlinearity and hysteresis in force-displacement diagrams. The main factor governing the transverse modulus is therefore considered to be not orientation texture but the amount of bonding between crystallites.

4.3. Transverse Compressive Strength and Appearance of Fracture

As shown in Fig. 4, no difference in the transverse compressive strength is found between random and radial fibers at similar L_c . Fracture paths of almost all fibers with large L_c observed under SEM run through the center of the cross section for both types of fiber. Strength is determined by the weakest area, as indicated by the presence of defects. Hence the center would be the starting point of fracture. Random and radial fibers were prepared from the same precursor and the similarity of the micro texture of their centers was deduced by the lack of difference in the transverse compressive strength.

The results of the torsional test showed a clear difference in micro texture between the two. However, torsional modulus is not sensitive over small areas and is determined more by the outer part than the core [13]. The test results therefore do not necessarily contradict the findings outlined above regarding the similarity of their micro texture.

In addition to the central area, the edge of the area of contact with the punch will be easily broken because shear stress caused by friction between the fiber and the punch is large there. In highly graphitized fibers, there will be many fragile places in all parts of the cross section as bonding strength between crystallites is weakened by graphitization, as described in 4.2. Fracture paths will thus initiated at the center to run through the edge of the contact area, as shown in Fig. 6.

When the fiber is not sufficiently graphitized, it can endure high load and released energy is large. Fracture paths will then follow complicated rather than simple lines. This explains why the less graphitized fiber broke into many pieces, as shown in Fig. 5.

5. CONCLUSIONS

Direct transverse compressive tests were carried out in pitch-based carbon fibers with randomly oriented and radially oriented textures. The transverse modulus and transverse compressive strength were calculated. The effect on these properties of the orientation texture of cross-sectional graphitic layer planes in pitch-based carbon fibers was discussed.

Although suggested by FEM analysis, differences in the

transverse modulus and transverse compressive strength were not found between random and radial fibers. Torsional tests of the fibers revealed the actual existence in the cross section of differences in the micro orientation texture of graphitic layer planes or crystallite orientation, in addition to the texture difference observed under SEM. The dependence of L_c on the transverse modulus and the nonlinearity of the force-displacement curve were considered to indicate that the dominant factor in the transverse modulus is not orientation texture but bonding between crystallites. SEM observations of transverse fracture from the loading axis and fiber axis indicate that the transverse compressive strength is determined by the micro texture in the central area, and suggested similarity in this regard between the random and radial fibers studied. Compared with longitudinal tensile properties, the transverse compressive properties are revealed to be less affected by orientation texture.

The authors thank PETCA, Ltd., for preparing pitch-based carbon fibers with special orientation textures.

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