論文

Mechanical Properties of C-And Hollow Shaped Pitch-Based Carbon Fibers

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C형 및 중공형 핏치계 탄소섬유의 기계적 특성

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초 록

열처리된 등방성 핏치로부터 C형과 중공형 노즐을 이용하여 C형 및 중공형 탄소섬유를 제조하여 형태인자, 산화시간, 화학증착 여부와 그에 따른 이들 섬유의 기계적 특성(인장강도, 비틀림강성)을 연구하였다. 산화시간과 섬유의 두께 변화는 탄소 섬유의 인장강도에 영향을 주었다. 등방성 핏치계 C형과 중공형 탄소섬유의 두께가 가늘면 가늘수록 인장강도가 증가하였다. 반면에 SiC가 코팅된 C형 및 중공형 탄소섬유의 인장강도는 섬유와 코팅층의 결합이 약하게 되어 증착시간이 증가할수록 감소되었다. 비틀림 강성은 섬유의 형태인자에 의해 영향을 받았으며, 중공형 탄소섬유의 비틀림강성이 동일한 형태인자를 가진 C형 탄소섬유 보다 더 컸다. 비틀림강성은 증착시간에 따라 증가되었는데, 이는 SiC 증착으로 인해 탄소섬유의 회전 빈도수가 증가되었기 때문이다.

ABSTRACT

C-and hollow shaped carbon fibers were prepared from heat-treated isotropic pitches through C-and hollow nozzles, respectively. The tensile strength and torsional rigidity of these fibers were studied with variation of shape factor, oxidation time, and CVD time. Tensile strength of the C-and hollow carbon fiber was affected by the oxidation time and the thickness of carbon fiber. The thinner the wall thickness of C-and hollow carbon fiber, the larger the tensile strength. On the other hand, the tensile strength of SiC-coated C-and hollow carbon fibers is decreased with increasing the CVD time, for the adhesion between fiber and coated layer become weak. The torsional rigidities of the C-and hollow carbon fibers were affected by the shape factor of carbon fiber, and the torsional regidities of the hollow shaped carbon fibers were higher than those of the C-shaped carbon fibers in the same shape factor. The torsional rigidity increased with increasing the CVD time, since the frequence of rotating shaft having SiC coated carbon fiber is increased.

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NOMENCLATURES

A_f : the cross sectional area of fiber[μm^2]
a : the circumference of a circle in Eq.(12)[μm]
b : thickness of the fiber in Eq.(12)[μm]
C_1 : constant in Eq.(12)
d_i : outside diameter of fiber[μm]
d_o : inside diameter of fiber[μm]
G : torsional rigidity[GN/m^2]
I : moment of inertia about the fiber axis of the suspended bar[kgm^2]
J : polar moment of inertia of the fiber [m^4]
L : fiber length[μm]
M_t : torsional moment
m : the mass of the bar[g]
r : radius of the fiber[μm]

Greek Letters

γ : vertical deformation rate
ν_c : natural frequence of vibration[sec^{-1}]
τ : shear stress[N/m^2]

1. Introduction

Pitch-based carbon fibers have been recognized as a strategic material for the near future because of their excellent tensile properties[1]. So, many studies on pitch-based carbon fiber preparation are being performed in order to improve the mechanical properties of pitch-based carbon fibers. Edie and Fain have shown that the mechanical properties were improved by the preparation of non-circular carbon fibers[2]. Metzler has repoted about hollow carbon fibers from various pitches [3], but he used C-shape nozzle successfully for hollow fibers. The tensile strength of a hollow carbon fiber from Japanese mesophase pitch(Kawasaki steel Co.) increased about 40% in comparision with that of Edie's results. Rhee et al.[4~5] studied more intensively with nozzle types and succeeded to spin not only C-fibers from C-nozzle but hollow fibers from various pitches. The mechanical properties, such as Young's modulus and tensile strength of carbon fibers, strongly depend on the precursor and the shape factor. The torsional rigidity and flexibility of the fibers were particularly varied with the shape of fiber even though the fibers were made from the same precursor. Outside diameter, inside diameter, and wall thickness of the fiber affect the polar moment of the fiber(shape factor). Fischbach et al.[6~7] studied the dynamic torsional behaviour of carbon fibers from PAN, rayon, isotropic pitch and mesophase pitch precursor with varing Young's moduls. In the case of rayon and pitch based carbon fibers, the torsional rigidity increased up to 30%, while PAN-based carbon fibers increased up to 50% according to the heat treatment temperature(1000℃~2700℃).

In this study, mechanical properties of C-and hollow pitch-based carbon fibers were investigated. Especially, the effect of oxidation time of as spun fibers and wall thickness of carbon fiber were investigated. For the evaluation of tensile strength and torsional rigidity, characteristics of SiC coated C-and hollow carbon fibers were studied as well.

2. Theoretical Backgrounds

2-1. Torsional rigidity

Torsional rigidity[8] can be determined quite simply by forming a torsion pendulum from a short vertical length of fiber cemented to the center of a horizontal inertia bar. The whole unit is quite small and a number of such pendulums can be mounted in an air-conditioned vessel placed in a thermostat for humidity and temperature control, and provided with means for starting the pendulums into oscillation. The rigidity modulus or storage modulus, G is given by

$$G = 4\pi^2 \ I \ L \ \nu_c^2 / J \qquad \cdots\cdots\cdots (1)$$

Where I is the moment of inertia about the fiber axis of the suspended bar, J is the polar moment of inertia of the fiber(shape factor), L is its length, and ν_c is the natural frequency of vibration.

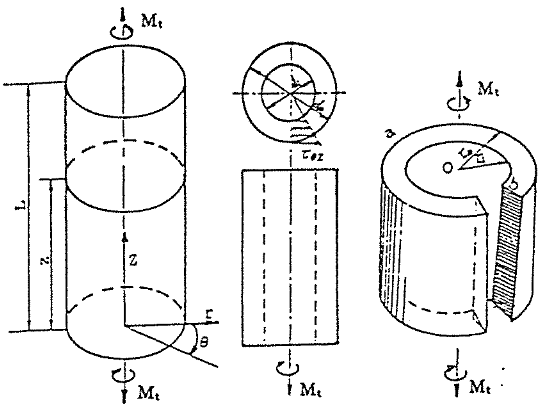
2-2. Deformation interpretation

The deformation of the pitch based carbon fiber under torsional force can be also interpreted by Hook's law. If the round shaped cylinder is deformed by a torsional force as Fig. 1, all vertical deformation rate become zero, that is

$$\rho_r = \rho_\theta = \rho_z = \gamma_{r\theta} = \gamma_{rz} = 0 \qquad \cdots\cdots\cdots (2)$$

If the material is deformed in the range of elasticity the shear stress are also

$$\rho_r = \rho_\theta = \rho_z = \tau_{r\theta} = \tau_{rz} = 0 \qquad \cdots\cdots\cdots (3)$$



(A) Round-shape (B) Hollow-shape (C) C-shape

Fig. 1. Deformation behaviour of various fibers under torsional force.

and by tension

$$\tau_{\theta z} = G\gamma_{\theta z} = Gr\frac{d\Phi}{dz} \qquad \cdots\cdots\cdots (4)$$

where the shear deformation rate from Fig. 1 is

$$\gamma_{\theta z} = \lim_{\Delta z \to 0} r\frac{\Delta\Phi}{\Delta z} = r\frac{d\Phi}{dz} \qquad \cdots\cdots\cdots (5)$$

The shear stress, $\tau_{\theta z}$ is caused by external force(Torsional moment)[9], therefore at equilibrium state

$$\Sigma M_t = M_t - \int_A r(\tau_{\theta z}\ dA) \qquad \cdots\cdots\cdots (6)$$

$$M_t = \int_A G(d\Phi/dz)r^2\ dA \qquad \cdots\cdots\cdots (7)$$

where G and $d\phi/dz$ are independent of the cross section.

Let define

$$\int r^2 dA \equiv J \qquad \cdots\cdots\cdots (8)$$

and if the rate of twist is constant, $d\phi/dz = \theta$

For the material with round cross section,

$$J = \int_A r^2 dA = \int_0^{do/2} r^2\, 2\, r\, dr \qquad \cdots\cdots\cdots (9)$$

For the annular cross section,

$$J = \int_A r^2 dA = \int_{d_i/2}^{d_o/2} r^2\, 2\pi\, r\, dr = \pi\ d_o^4(1-d_i^4/d_o^4)/32 \qquad \cdots\cdots\cdots (10)$$

For the C-shape cross section[10], suppose that the C-shape is equal to the rectangular-shape

$$J \fallingdotseq A_f^2 / 2\pi \qquad \cdots\cdots\cdots (11)$$

The maximum shear stress of rectangular shape is,

$$(\tau_{\theta z})_{max} = C_1\ M_t/a\ b^2 \qquad \cdots\cdots\cdots (12)$$

where, a = The circumference of a circle
b = Thickness

if $a/b \to \infty$, then constant C_1 become 3 approximately.

In this case

$$(\tau_{\theta z})_{max} = 3\ M_t/a\ b^2 \qquad \cdots\cdots\cdots (13)$$

Even though it is difficult to apply this equations to C-shaped fiber and hollow-shaped fiber directly, we can compare the value of torsional moments each other.

3. Experimental

Naphta cracking bottom oil(YUKONG) was treated by the process seen in Fig. 2 for isotropic pitch precursor. Table 1 shows the characteristics of this precursor : the softening point of isotropic pitch is 240℃. The isotropic pitch shows 1%-QI and 0%-O.A. The melt-spinning technique for the C-and hollow shaped fibers was described previously[5, 11]. And we used SiC coated C-and hollow shaped carbon fibers to compare mechanical properties. The CVD experiments were carried out a resistance heated apparatus, the details of which were described previously[12]. As an educt for deposition of SiC ; methy trichlorosilane(MTS, CH_3SiCl_3) was used and hydrogen with argon were used as carrier gases. SiC was deposited on the isotropic pitch-based C-and hollow carbon fibers. The uncoated as well as the coated fibers were characterized by their mechanical properties measured with Instron testing of monofilament. Fig. 3 shows apparatus used for measuring the torsional rigidity coefficent and modulus. The length of a

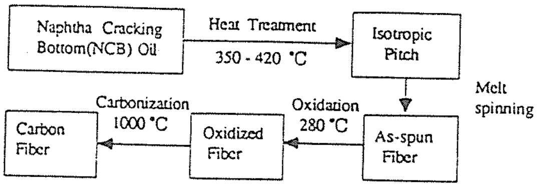


Fig. 2. Process for isotropic pitch-based carbon fibers.

Table 1. Characteristics of spinnable Pitch

Pitch proper-ties	S.P (℃)	Insolubles (Wt.)			Elemental Analysis(%)			O.A (%)
		HI	BI	QI	C	H	N	
Isotropic	240	91.6	48.3	1.1	97.1	2.75	0.12	–

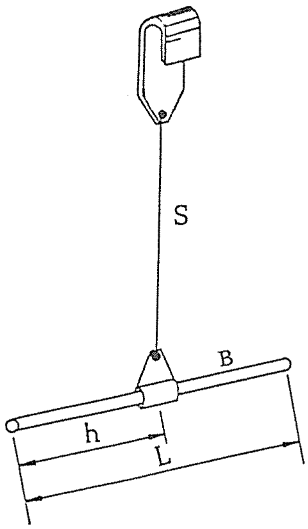


Fig. 3. Apparatus for measuring torsional rigidity.
S=Specimen, B=Suspended bar
L=0.025m, m=0.12g(mass)

specimen was approximately 25mm. Torsional rigidity was calculated with equation(1). In Fig. 3,

$$I = r^2\ dm = (1/12)m\ l^2 \qquad \cdots\cdots\cdots (14)$$

The I-value of the torsional equipment can be calculated from the equation(14). So, we calculated I with the measured data which m = 0.12g, $l = 2.5\times10^{-2}$m, and then we have

$$I = 6.25\times10^{-9}\ kgm^2 \qquad \cdots\cdots\cdots (15)$$

The as-spun fiber was oxidized at 280℃ with varying time. Heating rate was 1℃/min from 20℃ to 280℃. The stabilized fiber was carbonized at 1000℃ for 30min. The temperature was increased up to 1000℃ at the rate of 10℃/min from 300℃ in the nitrogen flow by the usual carbonization method.

4. Results And Discussion

4-1. Effect of oxidation time on the mechanical properties

In general, the tensile strength of carbon fibers were increased by oxidation up to the optimal oxidation time. The mechanical properties were chiefly related to the oxidation time if oxidation temperature was fixed at 280℃. The relationships between tensile strength and oxidation time of C-and hollow shaped filers are shown in Fig. 4 and Fig. 5. Thicker fibers require a longer oxidation time. They were fully oxidized when C-shaped carbon fibers with the wall-thickness of 3.5μm were heated to 280℃. At this condition, the onset tensile strength of these thin wall-thickness fibers were found to the maximum value of about 104.9 kg_f/mm^2. Then tensile strength decreased steeply. This phenomena is probably attributed to superoxidation. On the other hand, the tensile strength of the C-shaped carbon fibers with the thickness of 11.3μm increased with oxidation time up to 60min and further oxidation resulted in the decrease of tensile strength. That is, the time required to fully oxidized 11.3μm fibers is longer than that needed for 3.5μm fibers. In the case of C-shaped carbon fiber which have the wall-thickness of 21.0μm attained a maximum of 49.2 kg_f/mm^2 at oxidation time of 90min. The oxidation

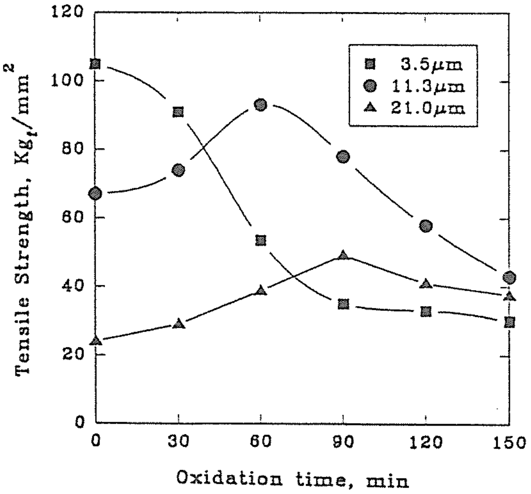


Fig. 4. Effect of the oxidation time on tensile strength of C-shaped carbon fibers with various thickness.

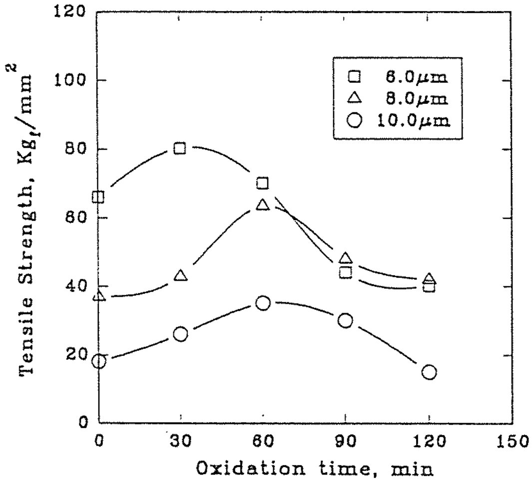


Fig. 5. Effect of the oxidation time on tensile strength of hollow-shaped carbon fibers with various thickness.

rate of fibers with the wall-thickness of 21.0μm is slowest and the tensile strength is also low. Though mesured value differ, the tendencies of tensile strength of hollow shape carbon fibers shown in Fig. 5 are similar to those of Fig. 4.

4-2. Effect of Wall-thickness on the mechanical properties

The relationship between the wall-thickness and the tensile strength of carbon fibers is shown in Fig. 6. The tensile strength of C-shaped carbon fibers is decreased from 104.6kg_f/mm^2 to 52.5 kg_f/mm^2 with the change of the wall-thickness from 9.5μm to 21.0μm. The tensile strength of Hollow shaped carbon fibers is decreased from 79.5kg_f/mm^2 to 44.1kg_f/mm^2 with the change of the wall-thickness from 6.0μm to 10.0μm, too.

The tensile strength of cabon fibers has been found to vary inversely with the wall-thickness of the fibers. Since the tensile strength is influenced by the presence of flaws, it could be inferred that the variation in strength with fiber thickness should be explained as a volume effect,

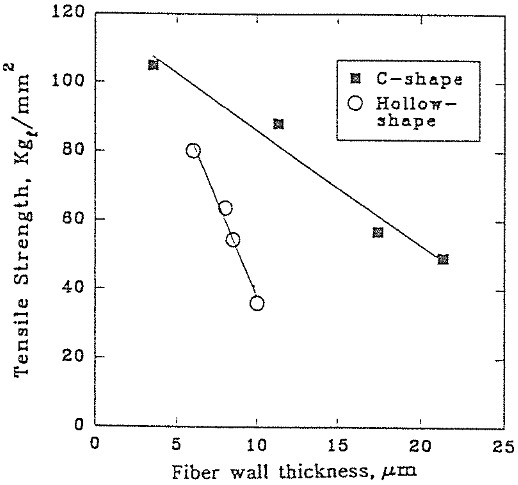


Fig. 6. Effect of the wall thickness on tensile strength of C-and hollow-shaped carbon fibers.

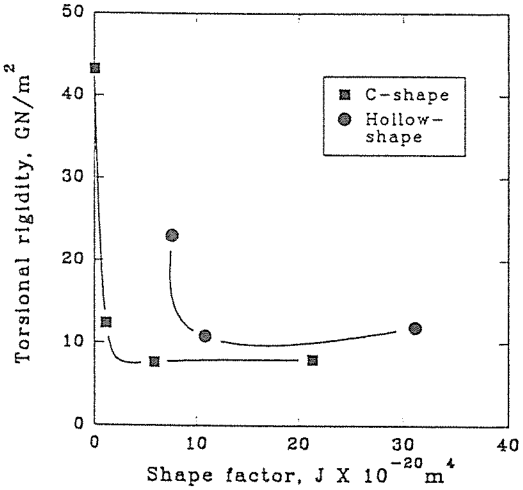


Fig. 7. Effect of shape factor on the torsional rigidity with the shape of the fiber.

since more flaws are expected to be present in a unit length of fiber for the thicker one. From this veiw point, it is believed that the decrease of wall-thickness of fibers clearly affected an increase of tensile strength.

4-3. Mechanical properties of uncoated and coated carbon fibers

For the variation of shape factor, winding speed, or stretching speed was controlled from 40m/min to 900m/min for C-shaped fibers and from 232 m/min to 586m/min for hollow shape fibers. With this variation, wall-thickness can be changed and shape factor(J) can be calculated from equations (10), (11). The frequences are measured by pendulum method and the torsional rigidities of carbon fibers are calculated with different shape factors.

Table 2 shows the measured and calculated data for isotropic carbon fibers, together with tensile strength. The torsional rigidities of the C-and hollow shaped isotropic pitch based carbon fibers were affected by the shape factor, and decreased exponentially as the increase of the shape factor of the carbon fibers shown in Fig. 7. As expected, the torsional rigidity of the hollow shaped carbon fiber was higher than that of the C-shape in the same shape factor.

Table 2. The torsional rigidity and tensile strength with the shape factor(J) in the isotropic pitch based carbon fiber

(a) C-shaped carbon fiber

Winding Speed m/min	Fiber thickness μm	Shape factor $J\times10^{-20}m^4$	Torsional ridigity GN/m^2	Tensile strength Kg_l/mm^2
40	21.3	20.14	8.0	49.2
80	17.4	5.83	7.5	56.8
300	11.3	1.13	12.4	88.1
900	3.5	0.013	43.2	104.9

(b) Hollow shaped carbon fiber

Winding Speed m/min	Outside diameter (D_o)μm	Inside diameter (D_i)μm	Shape factor $J\times10^{-19}m^2$	Torsional rigidity GN/m^2	Tensile strength Kg_f/mm^2
232	44.0	27.5	3.118	12.0	36.1
320	33.0	17.0	1.082	10.6	54.4
410	30.1	13.7	0.761	23.0	63.6
586	22.3	10.2	0.220	–	80.2

Torsional rigidities of SiC-coated carbon fibers are summarized in Table 3, in which the total pressure were 190mmHg and 760mmHg, and deposition time were 1, 2, and 6hrs, respectively.

Table 3. Mechanical properties of pitch-based carbon fibers coated with SiC

(a) C-shaped carbon fiber

Sample		Shape factor $J\times10^{-20}m^4$	Frequence ν_{c_1} sec	Torsional rigidity GN/m^2	Tensile strength Kg_f/mm^2
uncoated		2.359	1.58	7.228	83.5
190mmHg	1h		1.95	9.912	61.7
	2h		2.31	13.539	80.8
	6h		2.51	16.843	64.5
760mmHg	1h		2.32	14.074	60.7
	2h		2.98	23.221	73.1

(b) Hollow shaped carbon fiber

Sample		Shape factor $J\times10^{-19}m^4$	Frequence ν_{c_1} sec	Torsional rigidity GN/m^2	Tensile strength Kg_f/mm^2
uncoated		1.856	3.66	4.457	40.1
190mmHg	1h		4.57	8.654	30.5
	2h		8.26	19.213	35.6
	6h		9.93	32.770	26.7
760mmHg	1h		11.35	34.680	35.8
	2h		8.83	42.518	27.5

The average cross sectional area and diameter of C-shaped carbon fibers in these conditions were 390± 47μm^2 and 22μm, and those of hollow shaped carbon fiber were 1180± 161μm^2 and 39μm, respectively. These data show that torsional rigidity increased with increasing CVD time, as shown in Fig. 8 and Fig. 9. With the increase of CVD time, the frequence of rotating shaft having SiC coated carbon fiber is increased, and thus torsional rigidity is increased. The abnormal change of the tensile strength of coated carbon fibers might be attributed to the uniformity and thickness of the coated layers. The coating time of 1hr may not be sufficient to give the uniform covered surfaces of the fiber. And the uncoated layer acts as flaws and results in the substantial decrease of the tensile strength of the fiber. With the increase of the coating time, the surface of the fiber is fully covered by SiC-coated layer and uniform thin film is formed around 2hr, which is desirable condition for tensile strength. Thicker coated layer affects

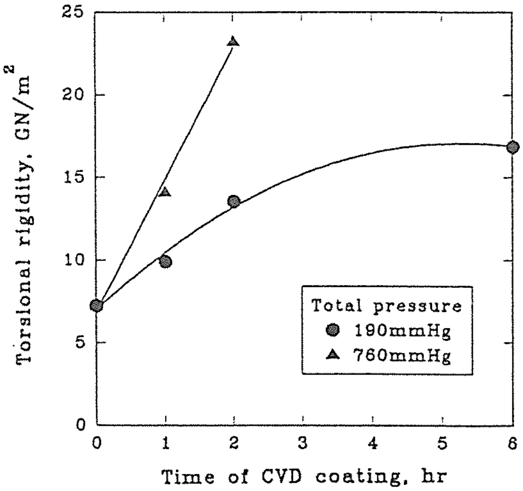


Fig. 8. Effect of time of CVD coating on torsional rigidity of C-shaped carbon fibers with the total pressure.

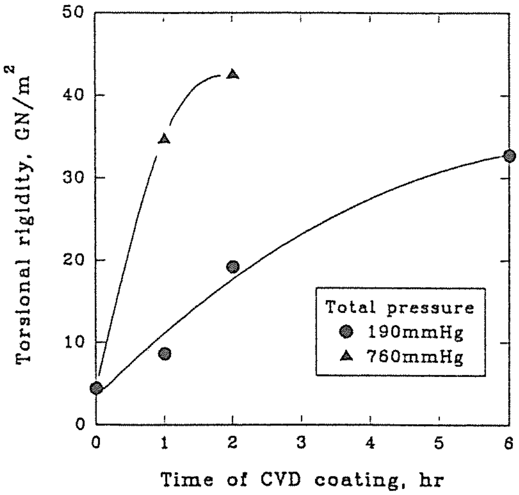


Fig. 9. Effect of time of CVD coating on torsional rigidity of hollow shaped carbon fibers with the total pressure.

again negatively the tensile strength of the fiber, which indicates that there exists the optimum thickness of the coated layer.

5. Conclusions

The mechanical properties of C-and hollow shaped pitch-based carbon fibers have been investigated. Especially, the effect of oxidation time of as spun fibers and wall-thickness of carbon fibers were investigated. For the evaluation of tensile strength and torsional rigidity, characteristics of SiC coated C-and Hollow carbon fibers were studied. The following experimental results are obtained.

(1) Tensile strength of the C-and hollow carbon fiber varied with oxidation time and thickness of carbon fiber. The thinner the wall-thickness of C-and hollow carbon fiber is, the larger the tensile strength appears, since more flaws are expected to be present in a unit length of the fiber in the thicker one.

(2) The torsional rigidities of the C-and hollow carbon fibers were affected by the shape factor of carbon fiber, and the torsional regidities of the hollow shape carbon fibers were higher than those of the C-shaped carbon fibers in the same shape factor.

(3) The torsional rigidity increased with increasing the CVD time, since the frequence of rotating shaft having SiC coated carbon fiber is increased.

(4) The tensile strength of SiC-coated carbon fiber is affected by the uniformity and the thickness of the coated layers. There exists a optimal CVD time to give fully covered fiber surfaces by SiC and optimized thickness of the coated layer.

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