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Characterization of differently shaped carbon fiber composites prepared from naphtha cracking bottom oil

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Abstract−Different shaped carbon fibers (R-, I-, C-, Y-, and X-type) were prepared from melt-spinning of reformed naphtha cracking bottom oil precursors through various shaped spinnerets. These different shaped CFs (carbon fibers) and PVC (polyvinyl chloride) resin were compounded, and then CF/PVC composites were prepared. Precursor pitch, carbon fibers, and composites were characterized and their properties were compared. Mechanical properties of carbon fibers and composites were characterized relating to external surface area and ratio of perimeter to cross-sectional area of carbon fibers. The tensile strength of tetralobal fibers (X-type) showed five times higher than that of round-shaped fibers (R-type) due to extended external surface area. Their tensile strength of CF/PVC composite increased as ratio of perimeter to cross-sectional area of carbon fibers. The magnitude of the ratio was in order to X-, C-, I-, Y-, and R-type.

Key words: Composite Materials Fibers, Petroleum, Process Control

INTRODUCTION

High strength and toughness, thermal and chemical stability, and light weight are very important characteristics of engineering materials. Carbon fiber, particularly high-performance carbon fiber is now widely demanded as a reinforcing filler of carbon/carbon composites [1,2].

Not only round-shaped carbon fiber but also carbon fibers of different shapes have been developed to improve mechanical properties. Edie et al. [3-5] have shown that the mechanical properties of pitch-based carbon fiber composites were improved by using C-shaped carbon fiber. The ribbon-shaped carbon fiber has excellent mechanical and thermal properties due to its aligned microstructure and texture. Thus, non round-shaped carbon fibers have gained increased attraction with improved mechanical properties and thermal conductivity [6,7]. However, there are not many researches on the preparation of carbon fibers of different shapes.

Spinning yield and fiber diameter were affected by molecular composition of precursor pitch and by the spinning conditions such as spinning temperature, pressure, and winding speed [8-10]. In general, precursor pitch with broad molecular weight distribution raised the spinning temperature, while narrow molecular weight distribution improved the spinnability [3].

The load transfer and shear of fiber-reinforcing composite are greatly dependent on the interfacial characteristics between matrix and reinforcing material, and three types of bonds (chemical, electrical, and mechanical bond) exist in the interface [11]. These interfacial bonds are able to affect the strength of composite, Young's modulus, shear strength, compressive strength and so on. In case of using the same reinforcing material and matrix, they can be affected by the mechanical properties because the chemical bond and electrical bond will be same.

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In this work, different shaped carbon fibers were prepared through various shaped spinnerets from pitch precursor, and CF/PVC composites were prepared with the fibers. Reforming and spinning conditions were investigated. Precursor pitch, carbon fibers, and composites were characterized and their mechanical properties were compared.

EXPERIMENTAL

1. Preparation of Different Shaped Carbon Fibers

Spinnable isotropic precursor pitch was prepared by reforming naphtha cracking bottom (NCB) oil at 380 °C, 3 h, following the previous work [12]. The softening point of precursor pitch was measured by using a Mettler FP 800 (USA). Molecular weight distributions of as-received NCB oil and precursor pitch were analyzed by MALDI-TOF (matrix-assisted laser desorption/ionization time of flight) mass spectrometry (Autoflex, USA).

The spinnerets, which have different hole shapes (R=round, I, C, Y, and X shape), were prepared and attached to the bottom of a melt-spinning cylinder. Fig. 1 shows the dimension of different shaped spinnerets. The cylinder containing reformed precursor pitch was electrically heated to the spinning temperature. Nitrogen was blown through the melted pitch to improve the fluidity and retain inert surrounding. As-spun pitch fibers were collected on a winding machine. The winding speed was adjusted in the range between 100 and 800 m/min, especially in consideration of fiber shapes. As-spun pitch fibers were placed in an air forced-convection oven and stabilized at 280 °C for 3 h. The stabilized fibers were cut into 5 cm length and carbonized at 1,000 °C, 0.5 h in nitrogen. The carbon fibers of different shapes were abbreviated to R-, I-, C-, Y-, X-CF, respectively.

2. Characterization

To study the degradation of fibers on temperature, thermogravimetric analyses of round-shaped fibers were measured by using a TGA 2050 (TA instruments, USA) in nitrogen condition. Average perimeter, cross-sectional area, and their ratio of different shaped

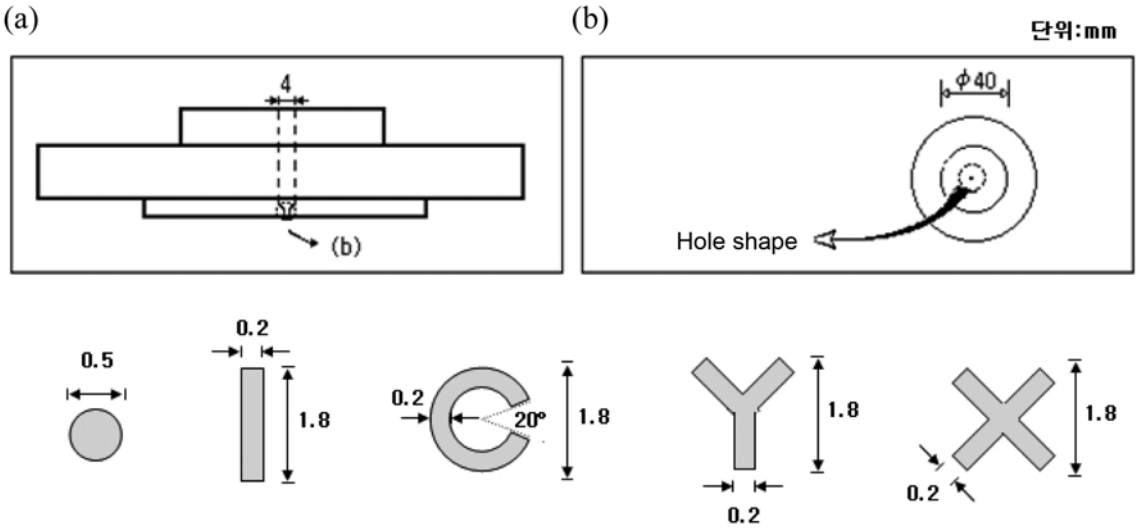

Fig. 1. Dimension of different shaped spinnerets. (a) a front view and (b) a plane figure.

Table 1. Properties of NCB oil and reformed precursor pitch*

	Softening point (°C)	Elemental analysis (wt%)				Molar ratio (C/H)	Density (g/cm^3)	Aromaticity (Fa)
		C	H	N	Diff.			
NCB oil	-	89.12	7.34	0.09	3.45	1.01	1.068	0.81
Pitch	247.2	93.84	4.57	0.18	1.41	1.71	1.051	0.89

*Reformed at 380 °C, 3 h

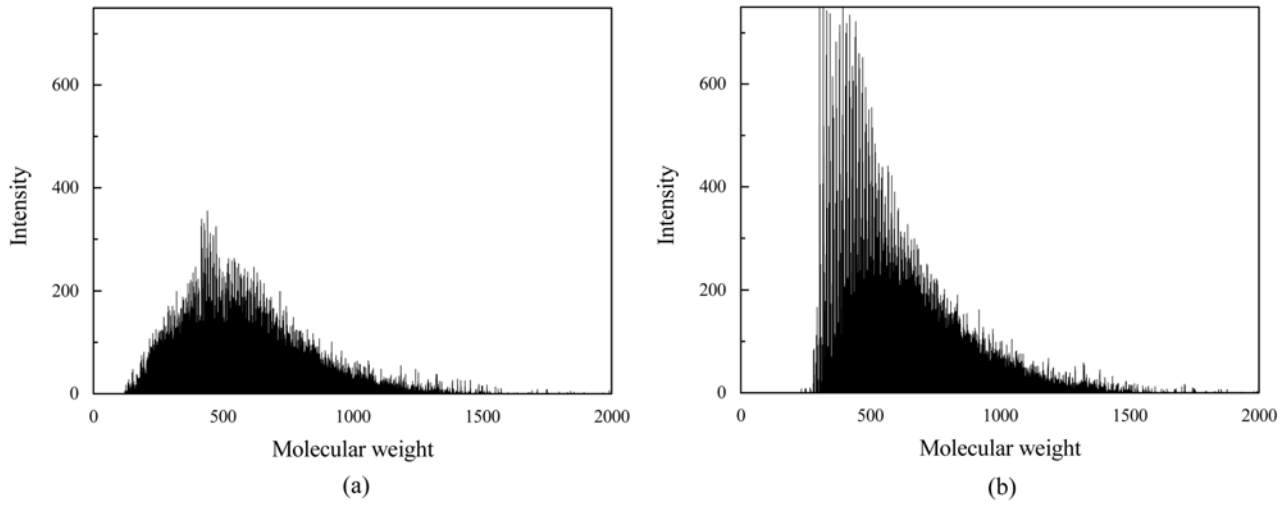

Fig. 2. MALDI spectra of (a) as-received NCB oil and (b) reformed precursor pitch.

fibers were calculated from at least 100 observations of scanning electron microscopy (TOPCON, SM-500) images. To investigate the mechanical properties of fiber type in composite, carbon fiber-PVC resin composites were prepared by ASTM D638 and their tensile strengths were measured by INSTRON (England).

RESULTS AND DISCUSSION

1. Preparation of Different Shaped Carbon Fibers

The properties of NCB oil and reformed precursor pitch are summarized in Table 1. The amount of hydrogen decreased, while carbon increased. Aromaticity also increased by heat reforming. Fig. 2 shows the molecular weight distribution of (a) as-received NCB oil, and (b) precursor pitch analyzed by MALDI-TOF. The molecular weight distribution of as-received NCB oil was broad showing in the range of 150-1,500. On the other hand, more than 80% of compounds were in the range of 350-850 after heat reforming, resulting in the increase of aromaticity. During the reforming of NCB oil, high molecular weight compounds were thermally degraded with producing volatiles and low molecular weight compounds were trans-

Table 2. Perimeter, cross-sectional area, and the ratio of perimeter to cross-sectional area of different shaped carbon fibers*

Shape	Spinning temperature (°C)	Perimeter (μm)	Cross-sectional area (μm^2)	Perimeter/ Cross-sectional area (μm^{-1})
R	294	91	660	0.138
I	295	148	928	0.159
C	298	219	1334	0.164
Y	297	229	1478	0.155
X	300	232	1339	0.173

*Spun at 400 m/min

formed to aromatic compounds by condensation reaction, which resulted in the narrow molecular weight distribution.

According to Kim et al., good spinnability of the pitch fiber from the precursor pitch was defined as continuous spinning over 1,000 m without breakage [12]. The optimum spinning temperature of the reformed precursor pitch showed good spinnability in the range of 294-300 °C (Table 2), which was approximately 50 °C higher than the softening point of the precursor pitch. The spinning temperatures of non round-shaped pitch fibers were similar to that of round-shaped pitch fiber despite different shapes of spinneret hole, which means that the spinneret shape did not much affect the spinning temperature.

Fig. 3 shows the diameter of the round-shaped pitch fiber as a function of winding speed. As the winding speed increased, the average diameter of the fiber decreased, whereas the total amount of the fiber remained constant. However, fiber breakage occurred frequently as the winding speed was over 800 m/min. When the winding speed was below 200 m/min, the desired shaped fiber could not be obtained due to the release of fiber tension before solidification.

Fig. 4 shows the SEM images of R-, Y-, and X-shaped fiber wound at 100 m/min and 400 m/min. When the winding speed was 100 m/min, fiber shapes were not clear. However, Y- and X-shaped fibers spun at 400 m/min were clear in shape. Accordingly, for fiber with the desired shape and spinning yield, the winding speed should be carefully adjusted depending on the spinneret shape [8]. Therefore, the winding speed was adjusted in the range between 200-500 m/min in consideration of fiber shapes.

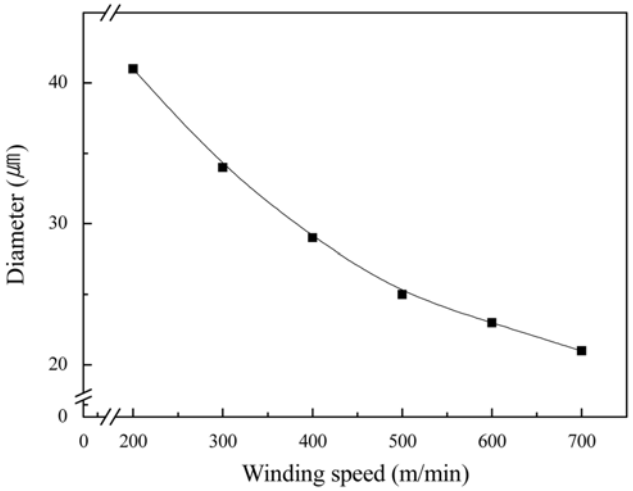

Fig. 3. The diameter of round-shaped pitch fiber as a function of winding speed.

Fig. 5 shows the thermogravimetric analysis of round-shaped pitch fiber, stabilized fiber, and carbon fiber. Gravimetric decrease in the mass of precursor pitch fiber and stabilized fiber began at around 340 °C. Thermostability of stabilized fiber increased by carbonization, because polymerization and condensation reactions occurred between carbon and carbon, and the gravimetric decrease was less than 5 wt% in nitrogen environment.

Fig. 6 shows the SEM images of different shaped carbon fibers.

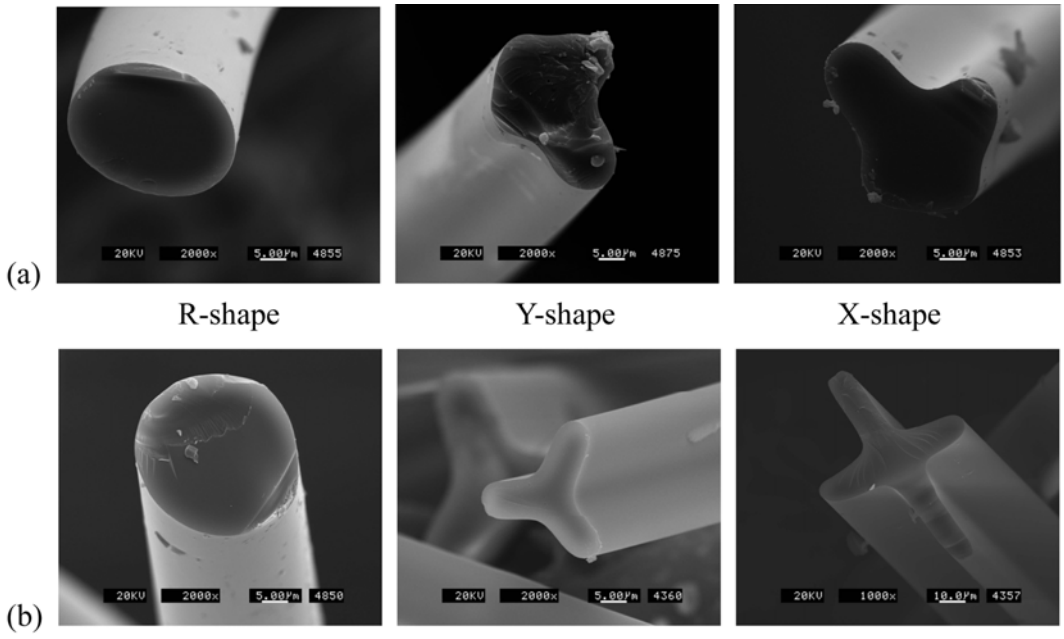

Fig. 4. SEM images of R-, Y-, and X-shaped fiber wound at (a) 100 m/min and (b) 400 m/min.

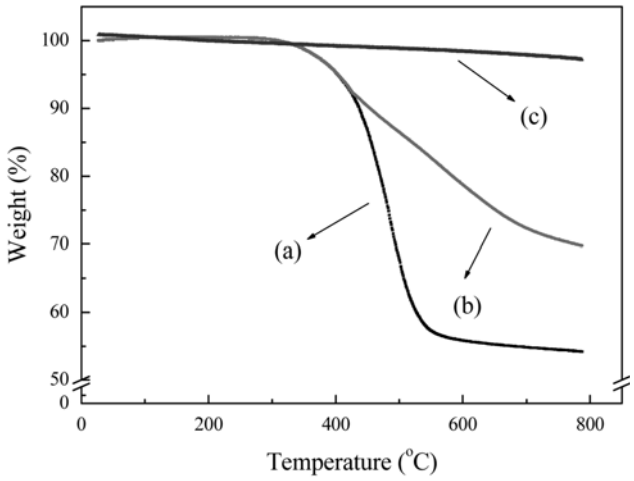

Fig. 5. TG analysis of round-shaped (a) pitch fiber, (b) stabilized fiber and (c) carbonized fiber in N_2.

Fiber shapes are very clear and uniform. Optical preparation conditions and method were described in sections 2.1 and 3.1. But these conditions and method must be changed by the operation machine and raw materials.

2. External Surface Area

Fig. 7 is a diagram of the cross sectional view of different shaped carbon fibers obtained from SEM images in order for calculation of external surface area of carbon fibers. D refers to the diameter of fibers and T refers to the length of minor axis of non-round shape fibers. The perimeter (P) and the cross-sectional area (A) of different shaped carbon fibers can be calculated by using the following equations:

Round-shaped carbon fiber:

$$P_R = \pi \cdot D_R, \quad A_R = \pi \cdot \left(\frac{D_R}{2}\right)^2 \tag{1}$$

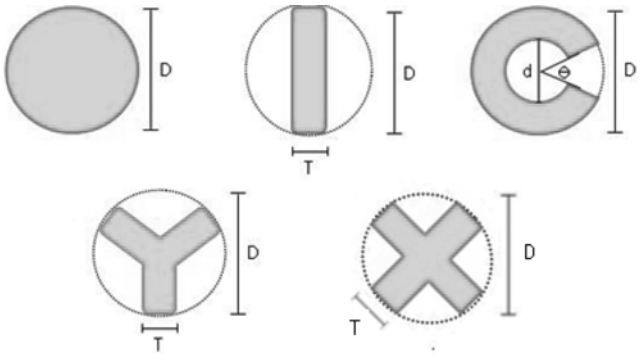

Fig. 7. Diagrams of several shaped carbon fibers.

I-shaped carbon fiber:

$$P_I = 2 \cdot (D_I + T_I), \quad A_I = D_I \cdot T_I \tag{2}$$

C-shaped carbon fiber:

$$P_C = \frac{360 - \theta}{360} \cdot \pi \cdot (D_C + d_C) + (D_C - d_C),$$

$$A_C = \frac{360 - \theta}{360} \cdot \frac{\pi}{4} \cdot (D_C^2 - d_C^2) \tag{3}$$

(θ is open angle)

Y-shaped carbon fiber:

$$P_Y = 3 \cdot D_Y - \sqrt{3} \cdot T_Y + 3 \cdot T_Y, \quad A_Y = \frac{3 \cdot D_Y \cdot T_Y}{2} - \frac{\sqrt{3} \cdot T_Y^2}{4} \tag{4}$$

X-shaped carbon fiber:

$$P_X = 4 \cdot D_X, \quad A_X = 2 \cdot D_X \cdot T_X - T_X^2 \tag{5}$$

If the cross-sectional areas are same for both R-CF and I-CF, the following equations can be expressed.

$$\pi \cdot \left(\frac{D_R}{2}\right)^2 = D_I \cdot T_I \tag{6}$$

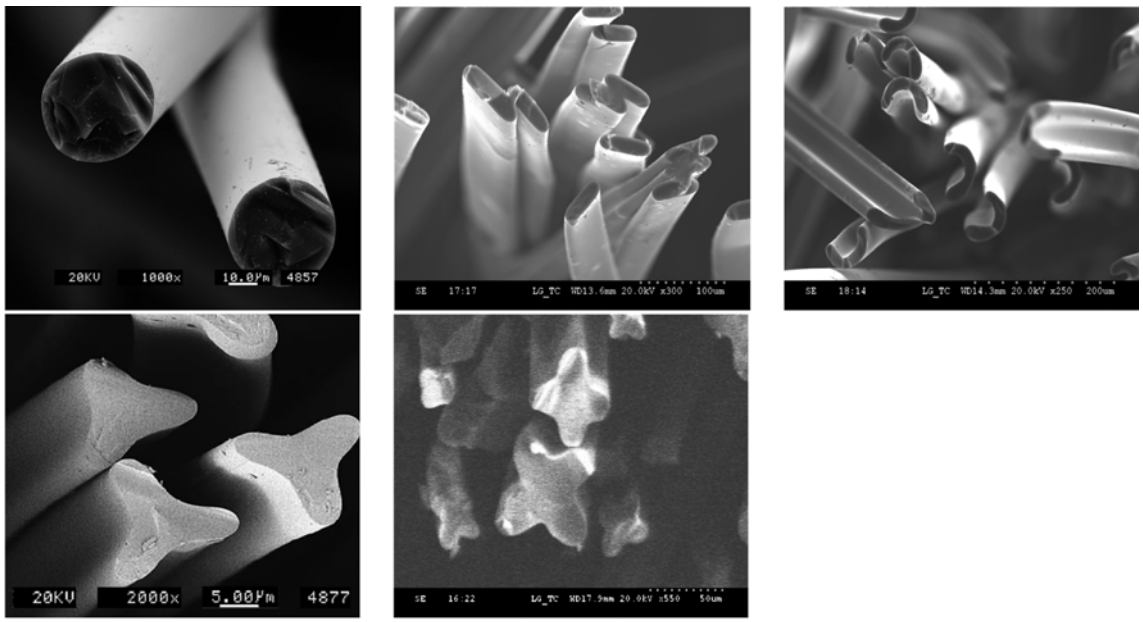

Fig. 6. SEM images of different shaped carbon fibers.

$$D_R = 2 \cdot \left(\frac{D_I \cdot T_I}{\pi} \right)^{0.5} \quad (7)$$

External surface areas (S) and the external surface area ratio of R-CF and I-CF are

$$S_R = \pi \cdot D_R \cdot L = \pi \cdot 2 \cdot \left(\frac{D_I \cdot T_I}{\pi} \right)^{0.5} \cdot L \quad (8)$$

$$S_I = 2 \cdot (D_I + T_I) \cdot L \quad (9)$$

$$S_{I/R} = \frac{S_I}{S_R} = \frac{D_I + T_I}{\pi \cdot \left(\frac{D_I \cdot T_I}{\pi} \right)^{0.5}} \quad (10)$$

α refers to the ratio of the diameter to the minor axis (D_I/T_I). Eq. (10) can be re-expressed as follows:

$$S_{I/R} = \frac{\alpha + 1}{\pi \cdot \left(\frac{\alpha}{\pi} \right)^{0.5}} \quad (11)$$

If α (D_I/T_I) is 5, which means that the diameter is five times as big as the minor axis, the external surface area of I-CF is 1.38 times bigger than that of the R-CF. According to the equation, **Pressure (flexural strength, stress)=Force (load)/Area**, I-CF can stand 1.38 times as much load than R-CF when the same force is given. In the same way, it is possible to compare different shape carbon fibers with R-CF.

By the way, we can assume that the total cross-sectional area (A) of any one type fiber is the summation of cross-sectional area of the individual fiber (A_s). Then the number of individual fibers (n_f) can be calculated by the following equation.

$$n_f = \frac{A}{A_s} \quad (12)$$

Also, the total external surface area (S) of any one type of fiber can be calculated by the perimeter of an individual fiber (P_s), number of individual fibers (n_f), and length (L).

$$S = P_s \cdot n_f \cdot L = \frac{P_s}{A_s} \cdot A \cdot L \quad (13)$$

Following the above equation, if the different shaped fibers have similar total cross-sectional areas and lengths, the fiber which has larger perimeter per cross-sectional area has larger external surface area. Therefore, the larger ratio of perimeter to cross-sectional area of carbon fiber is very meaningful for increasing the mechanical properties of composites.

Perimeter, cross-sectional area, and their ratio are summarized in Table 2. Perimeter and cross-sectional area of Y-CF were larger than those of others. But, the ratio of the X-CF is the largest and is approximately 1.3 times larger than that of the R-CF. Therefore, X-CF prepared under the same conditions might have approximately 1.3 times larger external surface area than R-CF.

Fig. 8 shows the cross-sectional area, perimeter and the ratio of perimeter to cross-sectional area of different shaped carbon fibers, depending on the winding speed. When the winding speed increases, the cross-sectional area and perimeter of fiber are usually expected to decrease. However, the perimeter of I-CF was almost constant, and those of C- and X-CF were increased. This is due to the thinning

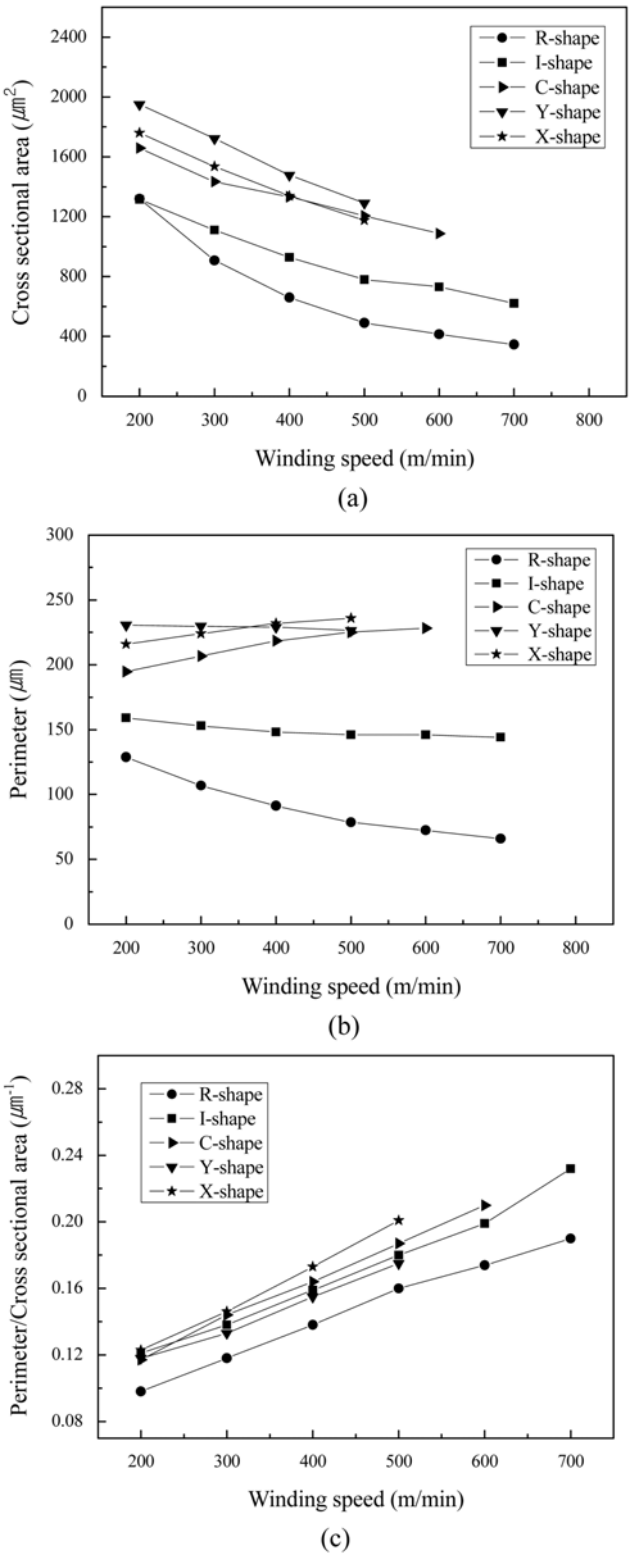

Fig. 8. (a) Cross-sectional area, (b) perimeter and (c) the ratio of perimeter to cross-sectional area depended on the winding speed.

of fiber thickness, and C- and X-shaped spinnerets have long perimeters. Therefore, in spite of the decrease of cross-sectional area and perimeter by increasing the winding speed, the ratio of perimeter

Table 3. Mechanical properties of different shaped carbon fibers and composites

Shape	Carbon fiber	CF/PVC composite*	
	Tensile strength (MPa)	Tensile strength (MPa)	Elongation (%)
R	40	15	491
I	74	15	472
C	123	16	453
Y	57	15	481
X	205	17	437

*Carbon fiber content; 3 wt%

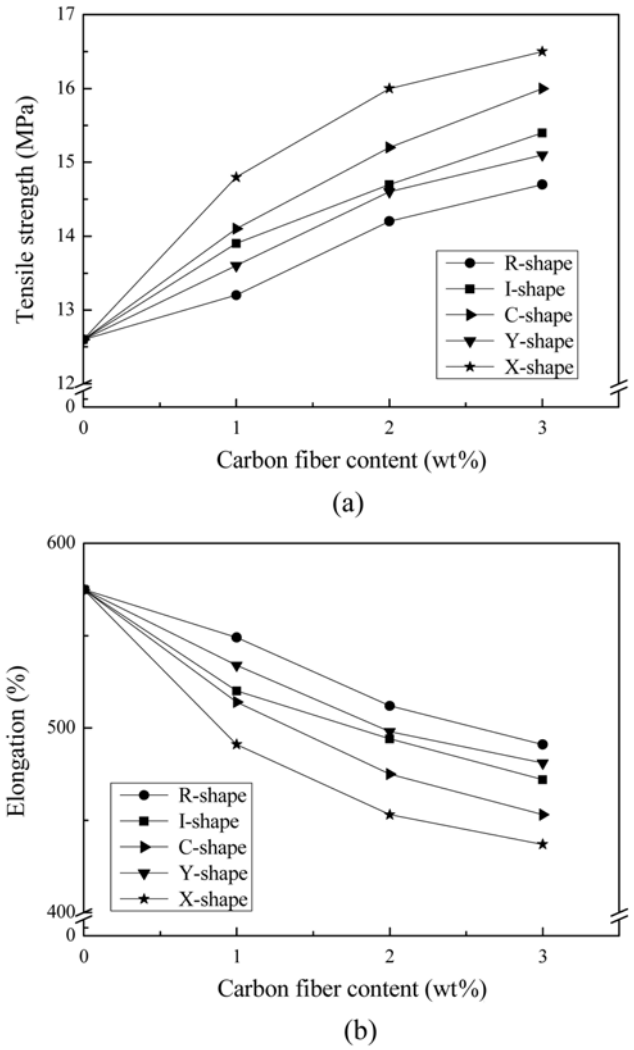

Fig. 9. (a) Tensile strength and (b) elongation of CF/PVC composites as a function of carbon-fiber content.

to cross-sectional area was increased; especially that of X-CF was the largest among the other carbon fibers.

3. Mechanical Properties of Different Shaped Carbon Fibers

Table 3 shows the mechanical properties of carbon fibers and composites. Tensile strengths of carbon fibers were in the range of 40-205 MPa. Particularly, tensile strength of X-CF was the highest among the other carbon fibers and was approximately five times higher than that of R-CF, which was due to the extended external surface area.

Fig. 9 shows the tensile strength and elongation of CF/PVC composites as a function of fiber content. Tensile strength of composite distinctly increased with the increase of fiber content, and the increase of ratio of perimeter to cross-sectional area at the same carbon fiber content. Particularly, in the case of the X-CF, the tensile strength of CF/PVC composite was the highest and the elongation was the smallest, which was due to the extended contact area between carbon fiber and PVC resin. Therefore, increased perimeter to cross-sectional area of carbon fiber is profitable to improve the mechanical properties of carbon fiber composite.

CONCLUSIONS

The average molecular weight distribution of reformed precursor pitch in this research was approximately 605 and more than 80% of compounds were distributed in the range of 350-850. Optimum melt-spinning temperature of different shaped fibers was in the range of 294-300 °C, and winding speed was in the range of 200-500 m/min. The tensile strength of the X-CF-reinforced composite was the highest of all the other composites due to the extended contact area between the X-CF and the resin matrix. The tensile strength of composite increased as ratio of perimeter to cross-sectional area of carbon fibers, and the magnitude of ratio was in order to X-, C-, I-, Y-, and R-type.

REFERENCES

1. J. B. Donnet, T. K. Wang, S. Rebouillat and J. C. M. Peng, *Carbon fibers*, Marcel Dekker, Inc. 3rd edition (1998).
2. T. J. Kang, S. J. Shin, K. H. Jung and J. K. Park, *Carbon*, **44**, 833 (2006).
3. D. D. Edie, *Carbon*, **36**(4), 345 (1998).
4. D. D. Edie, N. K. Fox, B. C. Barnett and C. C. Fain, *Carbon*, **24**, 477 (1986).
5. L. M. Manocha, A. Warrier, S. Manocha, D. D. Edie and A. A. Ogale, *Carbon*, **41**(7), 1425 (2003).
6. Z. Ma, J. Shi, Y. Song, Q. Guo, G Zhai and L. Liu, *Carbon*, **44**, 1298 (2006).
7. N. C. Gallego and D. D. Edie, *Composites*, **32**, 1031 (2001).
8. D. D. Edie and M. G. Dunham, *Carbon*, **27**(5), 647 (1989).
9. Y. V. Basova, D. D. Edie, Y. S. Lee, L. K. Reid and S. K. Ryu, *Carbon*, **42**, 485 (2004).
10. E. Mora, C. Blanco, R. Santamaria, M. Granda and R. Menendez, *Carbon*, **41**, 445 (2003).
11. K. Wolf, R. E. Forners, J. D. Memory and R. D. Gibert, *Chem. & Phys. of Carbon*, **18**, 93 (1982).
12. M. C. Kim, S. Y. Eom, S. K. Ryu and D. D. Edie, *Korean Chem. Eng. Res.*, **43**(6), 745 (2005).