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Mechanical Properties of C-type Mesophase Pitch-based Carbon Fibers

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Abstract

The C-type mesophase pitch-based carbon fiber (C-MPCF) was prepared throuch C-type spinnerette and compared the mechanical properties to those of round type mesophase pitch fiber (R-MPCF) and C-type isotropic pitch fiber (C-iPCF). The tensile strength and modulus of C-MPCF were about 18.6% and 35.7% higher than those of R-MPCF. The tensile strength of C-MPCF was 62% higher than that of C-iPCF of the same 8 μm thickness because of more linear transverse texture, which could be easily converted to graphitic crystallinity during heat treatment. The torsional rigidity of C-MPCF was 2.37 times higher than that of R-MPCF. The electrical resistivity of C-MPCF was 8 μΩ·m. The C-iPCF shows far lower electrical resistivity than R-iPCF as well as the mesophase carbon fiber because of better alignment of texture to the fiber axis.

Keywords : *MechaniCal Property, C-type Carbon Fiber, Mesophase, Electrical Resistivity.*

1. Introduction

Many studies are being performed in order to improve the mechanical properties of carbon fibers. They are including the processes of reforming of pitches, oxidation, carbonization, and so on. Edie and Fain [1] have shown that the mechanical properties of pitch-based carbon fibers were improved by preparation of non-circular type carbon fibers such as C-type and Y-type. Recently, Edie group [2, 3] reported the mesophase pitch-based ribbon type fibers of excellent mechanical and thermal properties arising from their special microstructure and texture. Because the graphene layers within carbon fibers tend to align parallel to the fiber axis, the mechanical properties and the axial thermal conductivity are strongly influenced by the same parameters which influence the mechanical and thermal properties of single crystal graphite. Fortin *et al*. [4] also reported that the mechanical properties of carbon fiber depended on the transverse alignment of graphene layers within slit-type carbon fiber. Thus, the perfection and degree of graphite crystallinity within the fiber is very important to mechanical and thermal properties of the fiber in the axial direction. The mechanical properties of fiber are also affected with the fiber thickness. Non-circular type carbon fibers can be used for special purposes such as high tensile strength materials and activated carbon fibers. Preparation of non-circular type pitch-based carbon fiber, especially thin thickness fiber, is not easy. However, authors have successfully prepared the isotropic pitch-based C- and Hollow type carbon fibers [5, 6].

In this study, isotropic and mesophase (anisotropic) pitch-based C-type carbon fibers were prepared, and compared with those of round type carbon fibers in terms of various properties.

2. Experiment

Spinnable isotropic pitch precursor was prepared by two step heat treatment [5] of naphtha cracking bottom (NCB) oil which was supplied from SK oil refinery company in Korea. NCB oil is liquid state at room temperature. For isotropic pitch precursor, about 4 kg NCB oil was heat treated from room temperature to 390^oC at a rate of 2^oC/min and held for 180 min., then cooled to 360^oC and held again for 180 min. For mesophase pitch precursor, similar volume of NCB oil was heat treated from room temperature to 390^oC at a rate of 2^oC/min and held for 180 min., then heated again to 430^oC at a rate of 1^oC/min and held for 30 min., and cooled to room temperature. Nitrogen was supplied during heat treatment, if necessary. The heat treated precursor pitches were melt-spun through round or C-type spinnerette. The thickness of C-type spinnerette is 0.2 mm which is the same to the diameter of round type spinnerette. The opening angle of C-type spinnerette is 10 degree. Matsumoto *et al.* [7] reported the effect of spinning conditions on structure of pitch-based carbon fibers including the length over diameter values of spinnerette. In this experiment, 1.5 mm length/0.2 mm thickness was applied as shown in Fig. 2.

Fig. 1 shows the schematic view of pitch-spinning system and Fig. 2 shows the design and size of C-type spinnerette. The diameters of round type carbon fibers and thickness of C-type carbon fibers depended on the winding speed of fiber. In this experiment, spinning of precursor pitches were performed as usual [5]. Optimum spinning temperatures of isotropic and mesophase pitch were 275^oC and 320^oC,

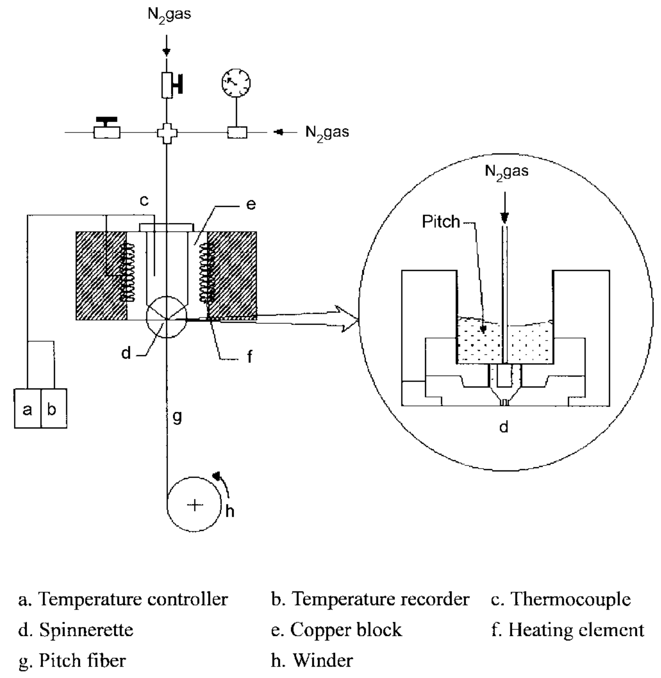

Fig. 1. Schematic view of pitch-spinning apparatus.

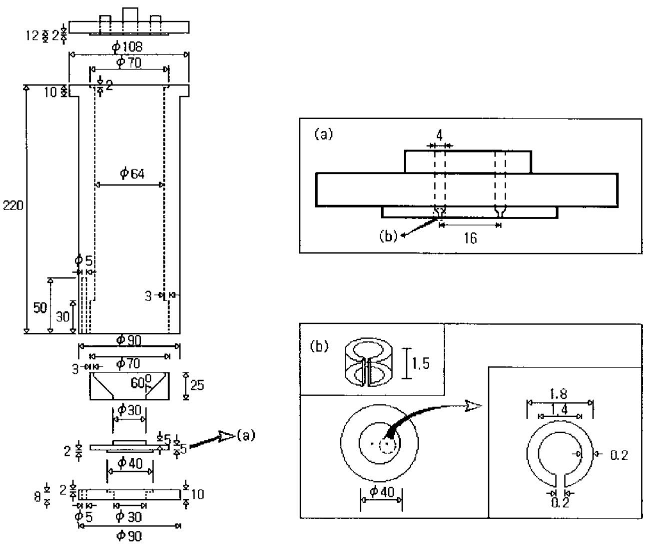

Fig. 2. Design and size of C-type spinnerette.

respectively. Winding speed was controlled by rotation of winding machine from 40 to 900 m/min of fiber length. The both round and C-type as-spun fibers were oxidized at 290 °C in air atmosphere, and carbonized at 1000°C in nitrogen atmosphere furnace. The mechanical properties of carbon fibers such as tentile strength and modulus were measured by a single-filament testing technique as described in ASTM standard D 3544-76. Torsional rigidity was determined by forming a torsion pendulum from a short vertical length of fiber cemented to the center of a horizontal inertia bar [8]. The electrical resistivity of fiber was measured by using a four point probe technique described by Coleman [9] and Edie *et al.* [10]. The cross-sectional area of each fiber was determined for both tensile measurements and resistivity using a mounting and image analysis procedure as described by Edie *et al.* [10].

Table 1. Properties of naphtha cracking bottom oil and precursor pitches

Pitches		NCB	Isotropic	Mesophase
Softening point (°C)		–	250	305
Specific gravity (g/cm^3)		1.068	1.20	1.60
Elementary analysis (wt%)	C	90.13	90	91
	H	6.85	5	4
	N	0.09	–	–
Atomic ratio (C/H)		1.1	1.5	1.9
Benzene insolubles (BI, wt%)		–	39.0	95.2
Quinoline insolubles (QI, wt%)		0.05	0.61	45.1
Hexane insolubles (HI, wt%)		–	95.0	–

3. Results and Discussion

The properties of reformed pitch precursors were compared with those of raw pitch in Table 1. The softening point of pitch increased with the increase of heating temperature and holding time at high temperature through polymerization of light molecular materials and depolymerization of large molecular materials. Large amount of benzene and hexane insolubles were formed in the isotropic precursor pitch. Quinoline insolubles were developed in mesophase pitch because of growth and coalescense of liquid crystal during high temperature heat treatment. However, the carbon contents of both precursor pitches were similar to that of raw pitch.

Photographs of round and C-type carbon fibers were shown in Fig. 3. Mesophase fibers show different textures in comparison with isotropic fibers. The graphene layers within mesophase pitch carbon fibers tend to align parallel to the fiber axis [3, 4]. The average outside diameters of C-type fibers were 27 μm for mesophase and 33.6 μm for isotropic carbon fiber at the winding speed of 300 m/sec. The inside diameters of both C-type fibers were 11 μm. Therefore, the thickness of both C-type fibers were 8.0 μm and 11.3 μm, respectively. The opening angle of C-type spinnerette is just 10 degree, but the average opening angle of C-type fibers was larger than 90 degree. This opening angle was continuously enlarged during oxidation and carbonization.

Table 2 shows the relationship between winding speed and C-type fiber thickness after oxidation and carbonization of as-spun fibers at the same conditions. Fiber thickness reduced remarkably by the increase of winding speed, especiallay for the C-MPCF. However, increasing the speed over 600 m/sec gave rise to frequent breakages of fiber. The thickness of both C-type fibers were not so much changed during oxidation and carbonization. In order to produce equal thickness fibers, the round fibers had to be extruded at a lower mass flow rate. Thus, the round fibers were melt-spun at a higher

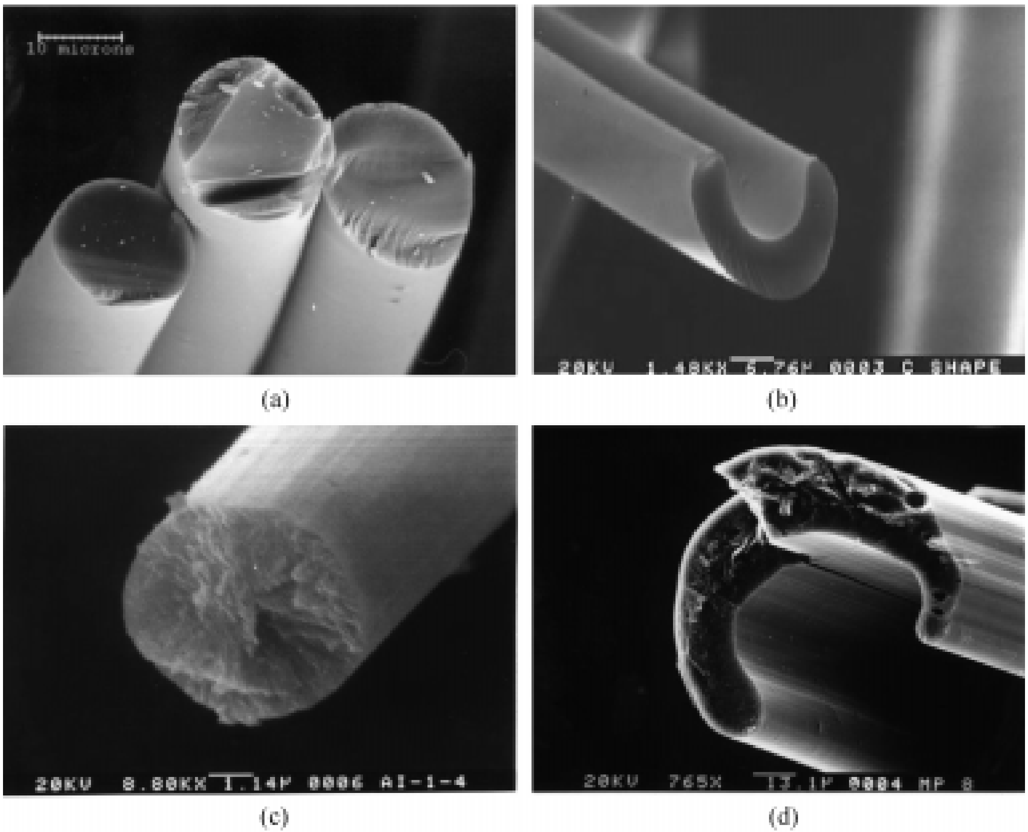

Fig. 3. Photographs of round and C-type carbon fibers. (a), (b): isotropic pitch-based, (c), (d): mesophase pitch-based

Table 2. Relationship between winding speed and thickness of C-type carbon fibers

Winding speed (m/sec)		40	80	300	600	900
Fiber diameter/ Thickness (μ)	C-iCF	22	17.4	11.3	8.0	3.5
	C-MPCF	21	17.5	8.0	5.5	–
	R-MPCF	22	15.0	11.0	7.5	–

i: Isotropic pitch, MP: Mesophase pitch

winding speed than the C-type fibers, which was the same to the results of Edie *et al*. [2].

Table 3 shows the mechanical properties of round and C-type pitch-based carbon fibers. The tensile strength and modulus of the C-MPCF were 18.6% and 35.7% higher than those of R-MPCFs. The torsional rigidity of C-MPCF was 2.37 times higher than that of R-MPCFs. These were resulted from the structural differences. It appeared that the superior mechanical properties of C-MPCF was a result of well aligned transverse texture, which could be easily converted to graphitic crystallinity during heat treatment. It has been shown that the transverse texture of a mesophase pitch-based fiber is generated during flow through the spinnerette or extrusion die and that subsequent drawdown orients the structure parallel to the fiber axis [11, 12]. This means the transverse texture of the resulting fiber can be altered merely by modifying the spinnerette design.

Holding time at 290°C for the oxidation of as-spun fiber affected the mechanical properties of final carbon fiber. Fig. 4 shows the relationship between tensile strength and holding time at 290°C for the oxidation of mesophase fibers. Tensile strength of both C-type and round type isotropic and mesophase pitch-based carbon fibers become maximum at 60min holding time for 8mm thickness fiber. The modulus of mesophase carbon fibers with respect to holding time were shown in Fig. 5, and the optimum holding time at 290

Table 3. Mechanical properties of round and C-type pitch-based carbon fibers

Precursor	CF-type	T S (kgf/mm^2)	T M (ton/mm^2)	T R (GN/m^2)	Density (g/cm^3)	Diameter/Thickness (μm)
Isotropic	R-iCF	95	5.5	-	1.65	22
	C-iCF	102	6.2	-		8.0
Mesophase	R-MPCF	145	18	5.1	1.78	11.3
	C-MPCF	172	28	12.1		5.5

Oxidation: 290°C, 60 min. Carbonization: 1000°C, 30 min.

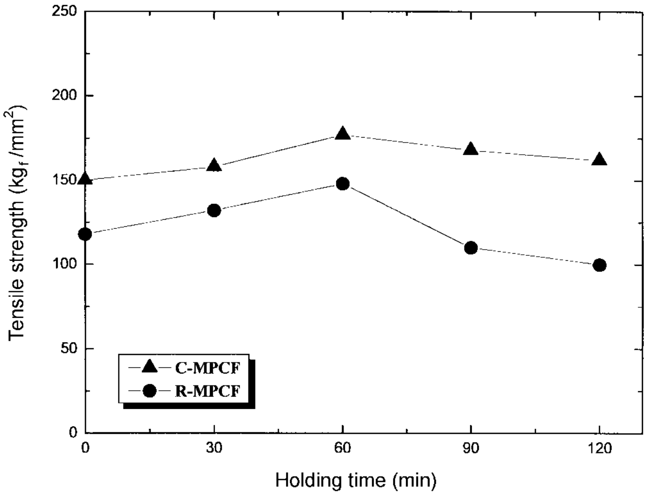

Fig. 4. Relationship between tensile strength of mesophase pitch-based carbon fiber and holding time at 290°C for 8.0 μm fiber thickness.

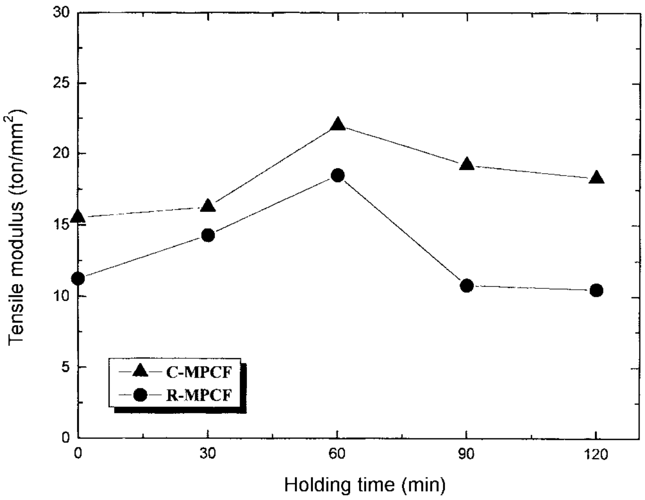

Fig. 5. Relationship between tensile modulus of mesophase pitch-based carbon fiber and holding time at 290°C for 8.0 μm fiber thickness.

°C was also recommended as 60 min for both types. However, the optimum holding time depends on the fiber thickness. Fig. 6 shows the relationship between tensile strength and holding time for different thickness of isotropic fiber. Thicker fibers require a longer holding time. This tendency is the same to general mesophase carbon fibers. The C-type carbon fiber shows higher tensile strength than round type carbon fiber at the same fiber thickness. Fig. 7 shows the relationship between tensile strength and fiber thickness at 60 min holding time. The tensile strength increased with the decrease of fiber thickness because of more linear transverse texture and uniform oxidation. The C-type mesophase pitch fiber shows stronger tensile strength than round type pitch fibers at the same thickness because of higher alignment to the fiber axis and degree of graphitic crystallinity within the fibers.

Table 4 shows the electrical resistivities of round and C-

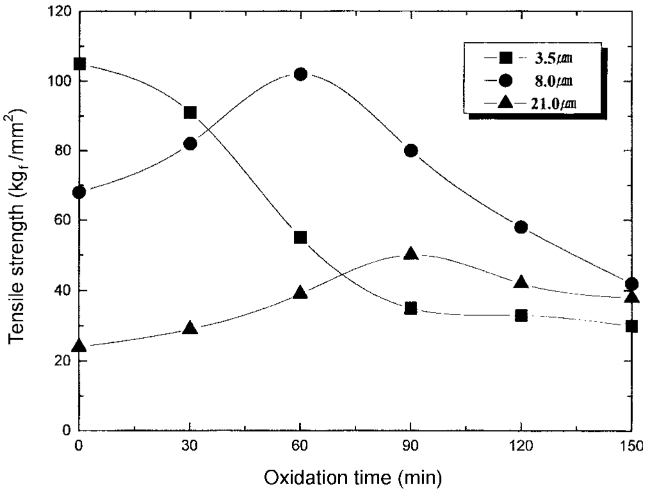

Fig. 6. Relationship between tensile strength of C-type isotropic pitch-based carbon fiber and holding time of oxidation at 290°C for different fiber thickness.

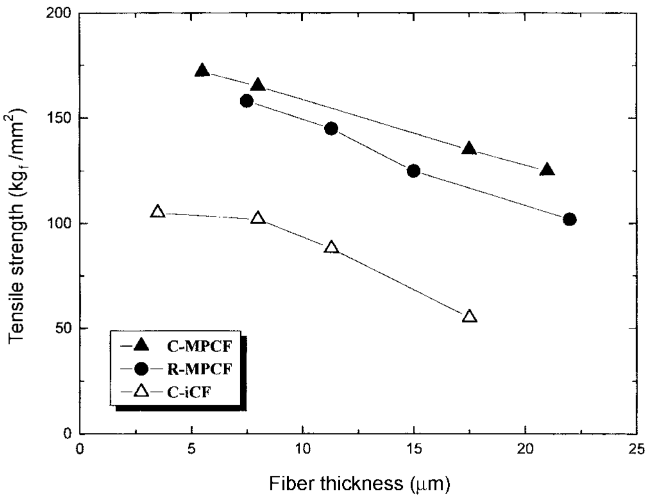

Fig. 7. Relationship between tensile strength and fiber thickness.

type isotropic and mesophase pitch- based carbon fibers. From the table, mesophase pitch-based carbon fibers show far lower elctrical resistivity than isotropic pitch-based carbon fibers because of fiber structure. Also, C-type fiber shows lower electrical resistivity than round type even though isotropic fiber. This results means that better alignment is formed in C-type fibers than round type fiber during the spinning of isotropic pitch and carbonization. The performance of both structural fibers and electronic systems often is limited by their ability to dissipate heat. Mesophase pitch-

Table 4. Electrical resistivities of round and C-type pitch-based carbon fibers

Fiber types	Isotropic		Mesophase	
	R-type	C-type	R-type	C-type
Electrical resistivity (μΩ · m)	97.1	38	11	8

based carbon fiber, with up to three times the thermal conductivity of copper, is an ideal material for reducing this thermal build-up. Lavin *et al*. [13] reported the correlation of thermal conductivity with electrical resistivity in mesophase pitch-based carbon fiber. Edie *et al*. [10] reported that ribbon shape mesophase pitch-based fiber shows about 7-9 μΩ·m of electrical resistivity, which is lower than 8-11 μΩ·m of Amoco & DuPont fiber. Edie and Fain [2] also reported that ribbon fiber from naphthalene-based mesophase shows 2.68 μΩ·m of electrical resistivity. Our mesophase pitch-based fibers show very similar electrical resistivity to Amoco & DuPont fiber. The C-type mesophase fiber shows lower electrical resistivity than round type mesophase fiber. This is because of more linear transverse texture of C-type fiber, which could be easily converted to graphitic crystallinity during heat treatment, increasing the electrical and thus the thermal conductivity of the carbon fiber. Therefore, the transverse texture of the resultant fiber can be altered merely by modifing the die design, and the C-type fiber can show more linear development of graphitic crystallinity to the fiber axis.

4. Conclusion

The C-type mesophase pitch-based carbon fiber was prepared throuch C-type spinnerette and compared the mechanical properties to those of round type mesophase carbon fiber and C-type isotropic pitch carbon fiber. The tensile strength and modulus of C-type mesophase fiber were higher than those of round type mesophase fibers because of more linear transverse texture of C-type fiber, which could be easily converted to graphitic crystallinity during heat treatment. The torsional rigidity of C-type mesophase fiber is 2.37 times higher than that of round type mesophase fiber. The electrical resistivity of C-type mesophase carbon fiber is also lower than that of round type mesophase fiber as following the same reason of linear transverse texture. The C-type isotropic carbon fiber shows far lower electrical resistivity than round type isotropic carbon fiber as well as the mesophase pitch-based carbon fiber. This means that better alignment is formed in C-type fibers than in round type fiber during the spinning of isotropic pitch and carbonization.

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