Preparation of Partial Mesophase Pitch-based Carbon Fiber from FCC-DO

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Abstract

Partial mesophase (PM) pitch precursor was prepared from fluidized catalytic cracking-decant oils (FCC-DO) by chemical reaction in the presence of Br_2. The PM pitch heated-treatment at 420°C for 9 h exhibited the softening point of 297°C with 23% yield, and 55% anisotropic content. The PM pitch precursor was melt-spun through circular nozzle by pressurized N_2, stabilized at 310°C, carbonized at 700°C, 1000°C, and 1200°C. The enough stabilization introduced 16.4% of the oxygen approximately. The stacking height (L_{c002}) and interlayer spacing (d_{002}) of the as-spun fibers were 4.58 nm and 3.45Å and the value became minimum and maximum at 700°C respectively in the carbonization procedure. The tensile strength increased with an increase in the heat treatment temperature exhibiting highest value of 750 MPa at 1200°C carbonization.

Keywords : FCC-DO, Bromine, Partial mesophase pitch, Carbon fiber

1. Introduction

The petroleum residues are mixtures of more than one thousand molecular compounds. Some of them are dominantly aliphatic or aromatic, exhibiting various aromaticity being essential to the production of cokes of acceptable industrial usage. The coking procedure contains several steps, which are nucleation, growth, and coalescence of mesophase spheres, finally into bulk mesophase [1, 2].

A decant oil (DO) from fluidized catalytic cracking (FCC) unit of petroleum refining process became currently one of the most important petroleum feed stocks for carbon precursors due to the low viscosity of consisting molecules with high H/C aromatic ratio at elevated temperatures.

A mesophase is developed through thermally induced dealkylation, dehydrogenation and subsequent condensation of medium sized aromatic hydrocarbons [3, 4]. The medium sized hydrocarbons endow mobility to stack and leading to the formation of mesophase. A good understanding of the relationships between mesophase development and the complex molecular composition of the petroleum feed stocks still remains as a current challenge, especially, in terms of predicting the quality of mesophase pitch from the petroleum feed stock of FCC-DO [4].

The pitch-based carbon fibers have been normally prepared from the precursors through the condensation of hydrocarbons with relatively low molecular weight, such as coal tar or petroleum residues. The key to the preparation of the mesophase pitch is how to prepare large enough molecules sustaining some mobility of the mesogens. Because the sources of the pitches consist of a large variety of hydrocarbon with various reactivities, a condensation of the species with low reactivity inevitably leads to the excess condensation of the more reactive species resulting infusible solids [2].

Singer *et al.* [5] developed a process for converting a low-cost isotropic pitch to more expensive mesophase pitch with a high yield of 50% exhibiting a softening point below 350°C. Rapid nitrogen flow reduced the content of non-mesogen species of low molecular weight inhibiting the mesophase formation. Chwastiak and Lewis [6] were able to produced a fully mesophase pitch through agitation of the reactive mixture and subsequent removal of the volatile components by inert gas flow.

Mochida and Mitsubishi Gas Chemical Co. [7] commercialized the spinnable mesophase pitch from aromatic (AR) hydrocarbons such as naphthalene or methyl naphthalene. The preparation of the mesophase pitch from AR compounds was carried out in the presence of $HF-BF_3$ at a relatively low reaction temperature (200-300°C), which was understood by the mechanism of cationic polymerization. The research was extended to the improvement of the compressive strength of the carbon fibers with the source of isotropic pitch containing mesophase spheres. The compressive strength of the fiber was doubled by the effects of fine fibrils attenuated from the small mesophase spheres along the fiber axis [8]. The similar approaches were performed to petroleum pitch precursor by Kato *et al.* [9]. They prepared carbon fibers with tensile strength of 4020 MPa through the formation of partial mesophase (PM) and subsequent removal of the extreme molecular sizes of the both ends.

Yang *et al.* [10-12] oligomerized coal tar or petroleum residual oil in the presence of *p*-nitroaniline [10], nitrobenzene (NB), halogens [11], or *p*-benzoquinone [12], to prepare precursor pitches for fiber spinning. They proposed that the mesophase could formed by reducing the reaction rate sustaining mobility for ordering among the consisting molecules.

In the present study, the pitch precursor of PM with appropriate softening point was prepared from FCC-DO through condensation reaction in the presence of Br_2. The PM precursor pitch was melt-spun smoothly and subsequently stabilized, carbonized. The mechanical properties of the fibers were tested and explained on the basis of microstructure of the sample developed in the preparation process.

2. Experimental

2.1. Preparation of mesophase pitch

The FCC-DO (SKC Co., Korea) was oligomerized in the presence Br_2 (Junsei Chemical Co. Ltd., first-grade) at a feeding rate of 0.1 ml/min in the reactor for 2 h at 110°C. The subsequent thermal aging was performed for 9 h at 420°C with a stirring speed of at 600 ± 50 rpm. The product was identified as F420-9 indicating thermal aged for 9 h at 420°C. The thermally aged pitches were cooled to room temperature under nitrogen flow and the product yield of precursor was calculated on the basis of the equation (1).

$$\text{Yield(\%)} = \text{weight of the precursor/} \\ \text{weight of the FCC-DO} \times 100 \quad (1)$$

For comparisons of the chemical characteristics, pyrolyzed fuel oil (Hanwha Chem. Co., Korea) and coal tar (KOSCO, Korea) were chosen.

The schematic diagrams of the reactor and the melt-spinning apparatus are shown in Fig. 1.

2.2. Preparation of carbon fibers

Precursor pitch was melt-spun by using pressurized nitrogen through a mono-hole spinneret (L/D=1, D=0.3 mm) 1 kg/cm² and at 335°C. The as-spun fibers were oxidatively stabilized in air for 2 h at 310°C and at heating rate of 2°C/min. The stabilized fibers were carbonized at 700°C, 1000°C and 1200°C for 1 h under Ar atmosphere at heating rate of 5°C/min. The carbon yield was calculated on the basis of the equation (2).

$$\text{Carbon yield(\%)} = \text{weight of the fiber carbonized/} \\ \text{weight of the fiber stabilized} \times 100 \quad (2)$$

2.3. Characterizations

Softening point was measured by using Mettler FP 90 apparatus (Mettler-Toledo AG, Switzerland, ASTM D3140).

Hexane insoluble (HI), benzene soluble (BS), benzene insoluble-pyridine soluble (BI-PS), and pyridine insoluble (PI)
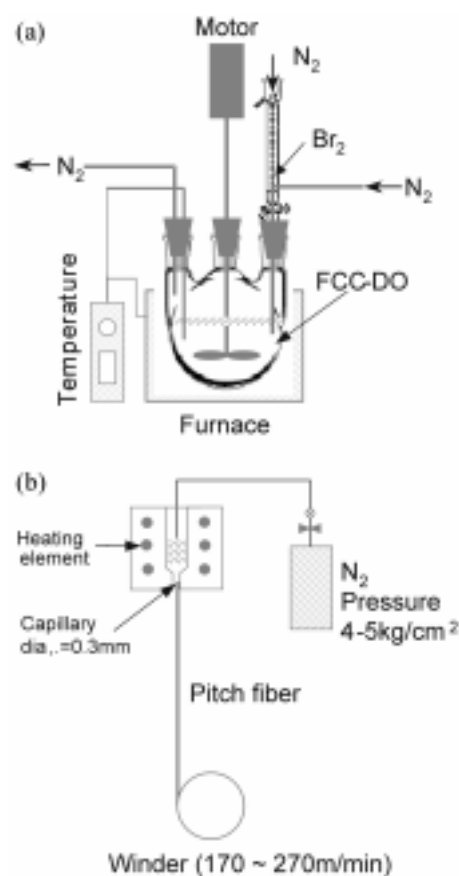

Fig. 1. Schematic diagram of (a)the reactor and (b)the melt-spinning apparatus.

portions of the pitches were measured by Soxhlet extraction method and the each fraction was calculated from taking fractions of the weight remained after the dissolution was completed.

Thermogravimetric analysis (TGA 1640, Stanton Redcroft, Canada) was performed under air or nitrogen atmosphere to find an optimum stabilization temperature or to measure the thermal stability of the samples, respectively.

The optical anisotropy of the mesophase containing samples were observed under a polarized-light microscope (AFX-II, Type-104, Nikon, Japan) after polishing the sample deposited in a unsaturated polyethylene terephthalate (PET) resin.

The fiber samples were fractured in liquid nitrogen and loaded on graphite paste to examine fracture surface by using SEM (Hitachi, S-4700, Japan).

C, H, N contents in a sample were determined from elemental analyzer(CE Instruments, Italy) and O content was determined from difference between the sum of C, H, N% and 100%.

The stack height (L_{c002}) and the interlayer space of carbon planes (d_{002}) of the fibers were calculated on the basis of Braun-lander and Bragg equations, respectively, from X-ray diffraction results (Dmax 1200, Rigaku; CuKα radiation, 40

Table 1. Some properties of pitches

Sample	Softening point (°C)	H/C ratio	f_a*	Elemental (%)			
				C	H	N	O
FCC-DO	Liquid at RT	1.05	0.71	89.74	7.88	0.48	1.90
PFO	Liquid at RT	0.95	0.82	93.31	7.42	0.02	0.75
CT	Liquid at RT	0.68	0.90	91.21	5.08	3.06	0.65

f_a*: aromaticity calculated on the basis of Brown-Lander equation

KV and 30 mA).

For tensile strength measurements, 2.5 cm sample was loaded and measured by using lab-scale tensile tester (Nano Technics Co, Korea) with a 150 g load cell at a cross head speed of 2.5 mm/min. An average was taken from the 5 tests on the basis to JIS R 7601 method.

3. Results and Discussion

The chemistry of the source material reflects not only on the behaviors of mesophase formation but also physical properties of the carbonized materials. The aromatic hydrocarbons with alkyl groups are normally characterized by the H/C atomic ratio, aromaticity and molecular size. Table 1 shows that FCC-DO exhibits highest H/C atomic ratio and lowest aromaticity among the samples chosen, which might be a source of high fluidity at elevated temperature. Pyrolyzed fuel oil (PFO) is another residue oil produced in the ethylene process and coal tar (CT) is a residue oil from cocking process.

The precursors for spinning at various heat-treatment conditions were summarized in Table 2. The higher temperature and the longer reaction time resulted in the higher softening point. The size of the consisting molecules seems to be unexpectedly large indicated by the high fraction of PI and low fraction of BS. And the relatively low fraction of BI-PS would introduce poor spinnability due to lack of the β resin reflecting processability.

The stabilization behaviors are dependent on the reactivity of the consisting molecules *i.e.*, the more pick-up of the oxygen representing the lower aromaticity. As shown in mass variations of Fig. 2, the oxygen picked-up started from
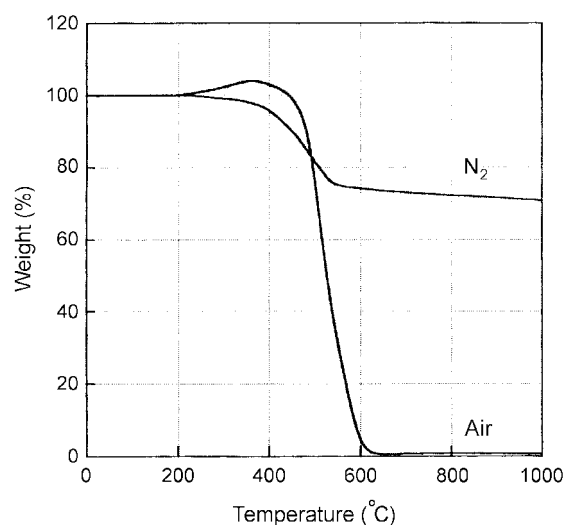

Fig. 2. The TGA curves of F420-9.

200°C and combustion evidently from 450°C. The thermal stability under nitrogen atmosphere indicated by the carbon yield above 600°C represents relatively high yield of 70%.

Elemental analysis data reflect chemical changes in the process of carbon fiber preparation (Table 3). The H/C atomic ratio decreases gradually with the increase in carbonization temperature and lengthen in treatment time. The stabilization introduced oxygen of 16.4% indicating the existence of relatively high concentration of alkyl groups.

The polarized light microphotographs visualizes the anisotropic properties of the mesophase and carbon fibers (Fig. 3). The F420-9 contains anisotropic spheres of 50~150 μm in the isotropic matrix. The 20 μm fibers spun from the precursors exhibited anisotropic stripes running along the fiber

Table 2. Some properties of PM pitches

Sample I. D.	Softening Point (°C)	A.C.[a] (%)	Solubility (%)			
			HI[b]	BS	BI-PS	PI
F420-9	297	55	97.6	16.3	5.9	77.8
F420-12	310	70	98.2	10.0	8.1	81.9
F425-8	297	63	98.3	10.3	6.9	82.8

A.C.[a]: anisotropic contents.
HI[b]. Hexane insolubles: BS. Benzene solubles: BI-PS. Benzene insolubles and pyridine solubles: PI. Pyridine insolubles.

Table 3. The elemental analysis of various conditions

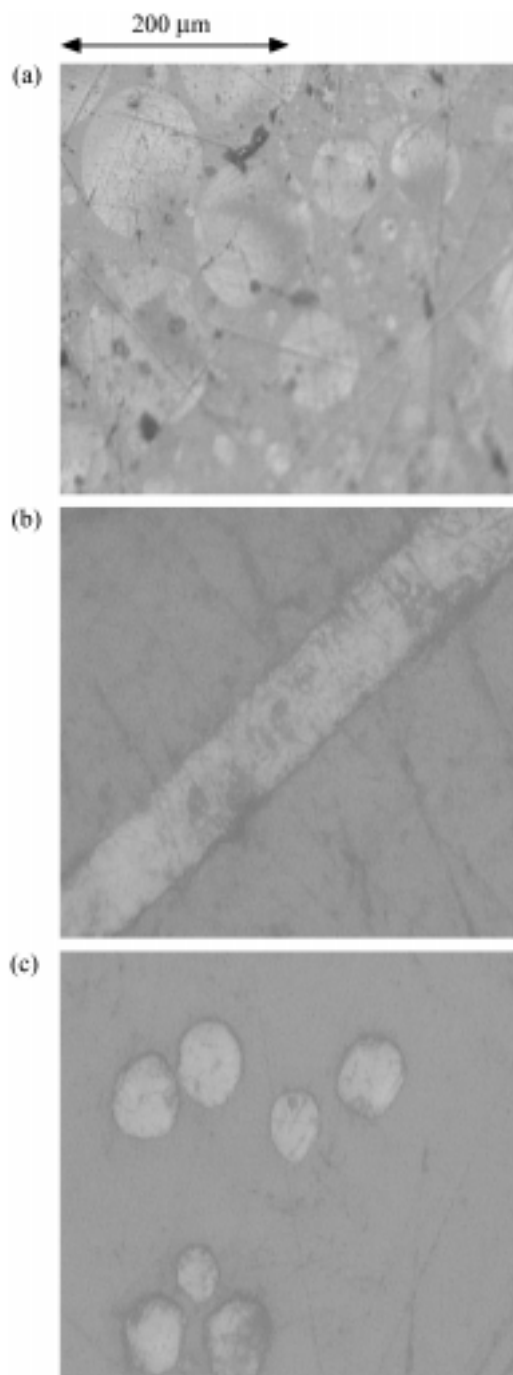| Sample	H/C ration	Elemental (%)			
		C	H	N	O
FCC-DO	1.05	89.74	7.88	0.48	1.90
F420-9	0.56	92.15	4.34	0.31	3.20
As-spun fibe	0.56	90.73	4.22	0.37	4.68
Stabilized fiber	0.43	80.24	2.89	0.44	16.43
Carbonized fiber	0.01	96.18	0.10	0.00	3.72

Fig. 3. The polarized light microphotographs of F420-9; (a) precursor, (b) the longitudinal surface of spun-fiber, and (c) the cross-section of spun-fiber.
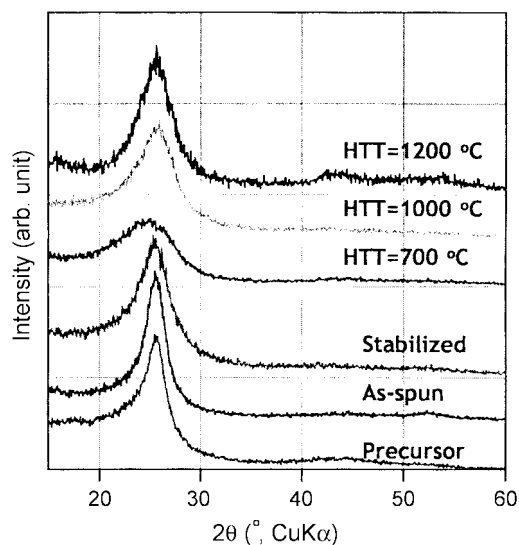

Fig. 4. The XRD curves of F420-9 at various conditions.
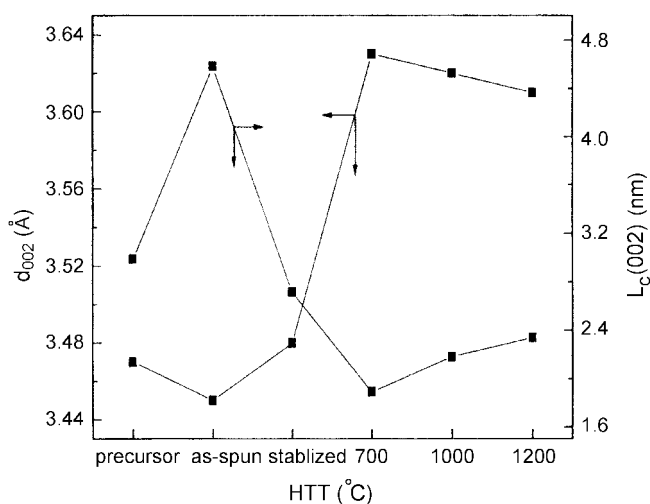
Fig. 5. The X-ray parameters calculated from Fig. 4.

axis. This indicates that the shear stress deformed the anisotropic sphere in the spinneret and subsequent extension along the spinning line. The fibrils in the carbonized fiber was identified with consisting of pleat units [13].

The microstructure of the carbonfibers changes sequentially along with the procedure (Figs. 4 and 5). The L_{c002},

was increased by attenuating the mesophase spheres in the process of spinning, and decreased by randomization through the oxygen insertion between the consisting layers, minimum at 700°C heat-treatment due to further randomization in the process of gas evolution and also thermal energy, and started to increase again with further carbonization. The interlayer spacing behaved in the opposite direction from the L_{c002} value.

Fig. 6 shows the SEM microphotographs of the fibers treated at various conditions. The carbonized fiber at 700°C, and 1200°C exhibited typical radial-core structure [14].

Fig. 7 shows the fracture surface of cross-sectional area of the carbon fiber including remained domains without attenuation in the spinning process as indicated by the arrows. Normally the non-attenuated domain in the fiber causes deterioration of mechanical properties of the fiber. The constituent domains were separated as anisotropic and isotropic in the
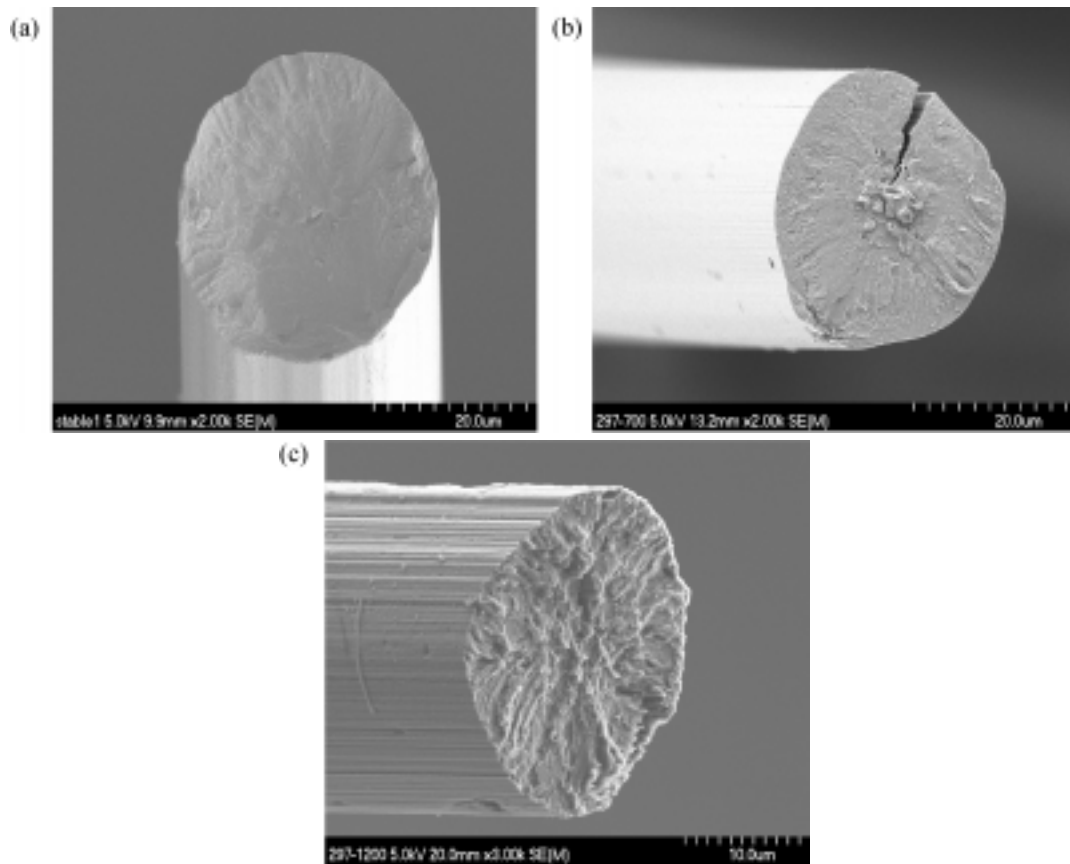
Fig. 6. The SEM microphotographs of the fibers treated at various conditions; (a) the stabilized fiber, (b) the carbonized fiber at 700ºC, and (c) the carbonized fiber at 1200ºC.
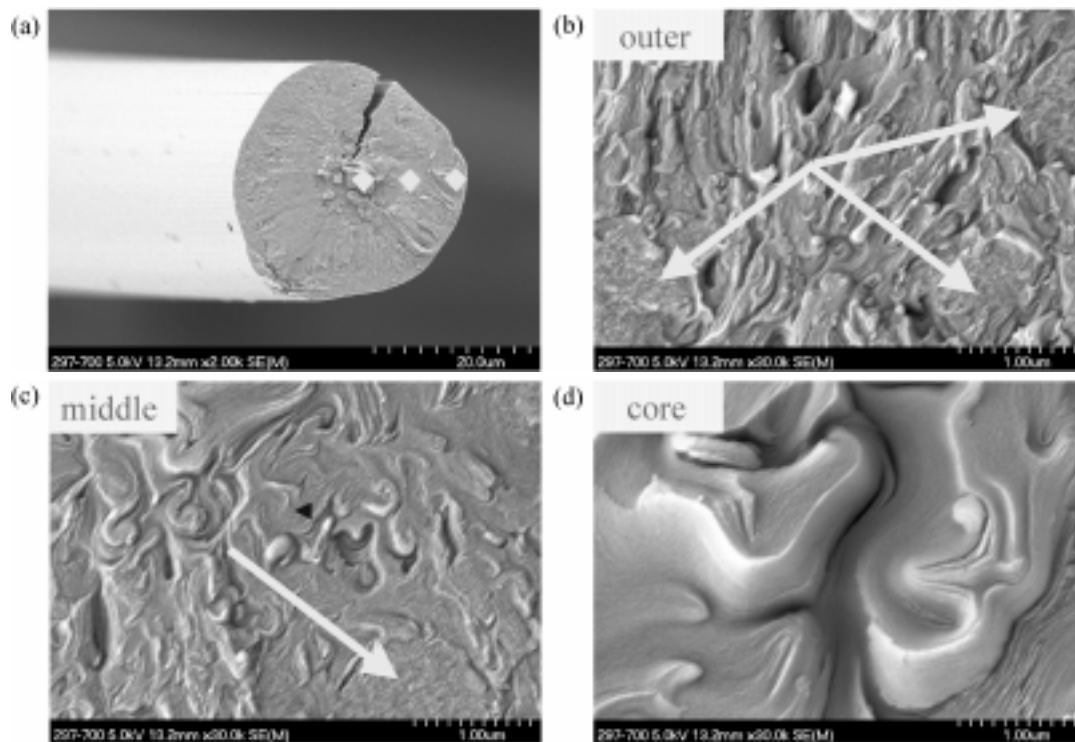

Fig. 7. The fracture surface of cross-sectional area of the carbonized fiber at 700ºC, non-attenuated domains indicated by arrows.
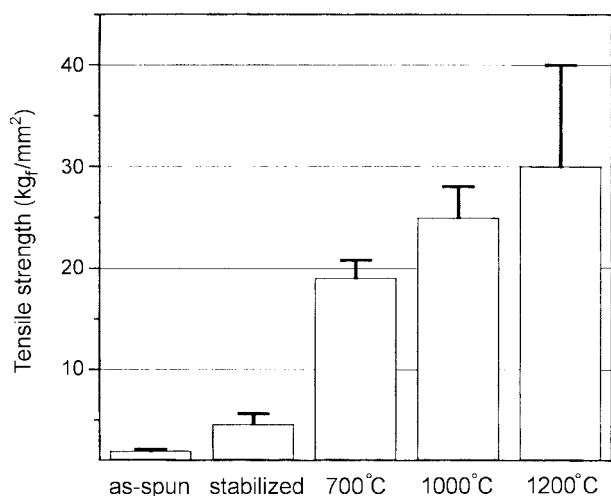
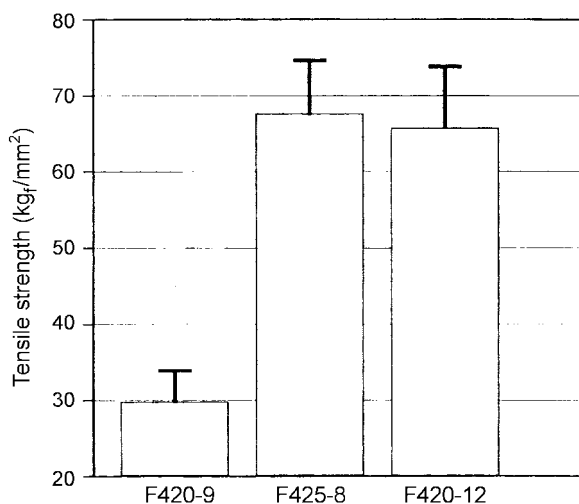Fig. 8. The tensile strength of the carbon fibers at various conditions.

Fig. 9. The tensile strength of the precursor variations carbon fibers carbonized at 1200°C.

texture as shown in Fig. 3. The anisotropic shapes of the outer, middle, and core area were typically linear, bent, and loop, respectively. It is considered that the shapes and alignment of the domains are dependent upon the spinning conditions and the properties of precursor pitch [15].

The tensile strengthes of the as-spun, the stabilized, the carbonized fibers at 700°C, 1000°C and 1200°C were represented (Fig. 8). The precursor variations resulted different tensile strengths as shown in Fig. 9. F425-8 carbon fibers carbonized at 1200°C showed the highest tensile strength upto 750 MPa among fibers tensile properties tested.

4. Conclusions

PM pitch precursor was prepared from FCC-DO by chemical reaction in the presence of bromine. The precursor was melt-spun, stabilized, carbonized. The morphological structure and mechanical properties of the fibers were examined. The major results obtained are as follows:

1. The PM precursor with 55% of anisotropic content was prepared with softening point of 297°C, 23% yield on the base of raw FCC-DO.

2. The PM pitch precursor showed good spinnability with wind-up of 270 m/min.

3. The carbonized fiber at 1200°C exhibited the tensile strength of 750 MPa.

4. Typical radial-core structure was formed through carbonization of the fiber at 1200°C.

Acknowledgment

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