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Mesophase pitch and its carbon fibers

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Abstract
Mesophase pitch-based carbon fiber is expected to exhibit high tensile properties due to its high oriented molecular structure and high crystallinity of graphite. They can be prepared at a low-cost because of their cheap raw materials and high carbon yield. Mesophase pitch carbon fibers have a wide variety of internal structures, such as radial, random, onionskin and their intermediates. The internal structure is determined by the shear conditions in the spinneret and the dimensions of the die. To obtain proper structures and, as the result, high tensile properties, it is most important to control the spinning process since molecular orientation of mesophase pitch is determined almost exclusively in this process.

INTRODUCTION

Carbonization of fiber was first applied by the Edison in his process of obtaining incandescent filaments about a century ago and is now an essential process in the carbon fiber production. Carbon fibers are unique materials and have a wide variety of applications. Especially high performance carbon fibers (HPCFs) have recently gained considerable attention and are used as a reinforcing component of the advanced composite materials for aerospace application and sporting equipments. These applications of HPCFs are based on their high strength and high modulus, which are attributable to the structure of highly oriented hexagonal carbon-carbon networks, similar to that of single crystal graphite. A comparison of some different types of carbon fibers in precursor is described in the next section. The main emphasis of this paper will be on the spinning of mesophase pitch. Dependence of the transverse structure of mesophase pitch-based carbon fibers on the shear conditions in a spinneret and on the dimensions of a die used for the melt spinning procedure is also described.

COMPARISON OF CARBON FIBERS

In order to obtain carbon fibers with desirable properties, a wide variety of organic materials have been investigated for their use as precursors during the past decades. Mainly rayon, polyacrylonitrile (PAN), and carbonaceous pitch have been used in the industry as the precursors for carbon fibers.

Some properties of carbon fibers supplied by manufacturers are shown in Table 1. The tensile strength of PAN (T800) and the tensile modulus of mesophase pitch (P120) are remarkably higher than others. The tensile properties of rayon are nearly equal to PAN M50 (graphitized fiber). However, as shown in Table 2, rayon and isotropic pitch require to be subjected to a hot stretching procedure at a high temperatures to obtain a highly oriented structure and, accordingly, a high modulus (ref. 1-3). In contrast, anisotropic mesophase pitch itself has a highly oriented structure and can be subjected directly to carbonization without such inconvenient and less economical treatment needed for rayon and isotropic pitch. Thus, currently, PAN and mesophase pitch are preferentially employed as precursors for HPCFs. Especially, mesophase pitch is expected to have better characteristics as the precursor of HPCFs than PAN because of its higher "graphitizing" characteristics.

In case of mesophase pitch-based HPCF, tensile modulus of 830 GPa can be attained, which is equivalent to 80% of the theoretical value for graphite crystal. In contrast, the maximum value of the modulus attained for PAN-based fibers is considered to be about 500 GPa. Figure 1 shows the tensile properties of manufactured PAN- and mesophase pitch-based carbon fibers. Mesophase pitch-based carbon fibers have a higher tensile modulus than PAN, while the tensile strength of mesophase pitch carbon fibers are much lower than that of PAN. However, the tensile strength of a carbon fiber depends on its elongation which, in turn, is determined by the degree of defects. When the elongation is constant, fibers with higher modulus exhibit the higher strength. For this reason, mesophase pitch-based carbon fibers are expected to exhibit higher tensile strength and modulus than PAN, if the defects in carbon fibers can be removed sufficiently. Furthermore, the higher carbon yield from mesophase pitch (Table 2), in addition to the cheaper raw material, suggests the possibility that mesophase pitch-based carbon fibers are prepared at a lower cost than PAN.

Table 1. Properties of carbon fibers derived from various kinds of precursors

		Density (Mg/m^3)	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation (%)	Electrical resistivity (μOhm·m)
Rayon 1)	50S	1.67	1.9	390	0.5	10
	75S	1.82	2.5	520	0.5	—
Polyacrylonitrile 2) (PAN)	T800	1.80	5.6	290	1.9	13
	M50	1.91	2.4	490	0.4	7.6
Isotropic pitch 3)	T101F	1.65	0.8	33	2.4	150
	T201F	1.57	0.7	33	2.1	50
Mesophase pitch 4)	P25	1.90	1.4	160	0.9	13
	P120	2.18	2.2	830	0.3	2.2
Single-cristal 5) graphite		2.25	—	1000	—	0.4

1) Union Carbide, Thornel R.
2) Toray, Torayca R.
3) Kureha.
4) Union Carbide, Thornel R.
5) Modulus and electrical resistivity are in-plane values.

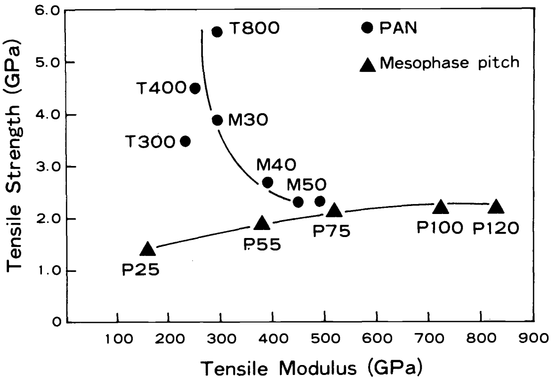


Fig. 1. Tensile properties of manufactured PAN- and mesophase pitch-based carbon fibers.
PAN (Toray Ind., Torayca™)
Mesophase pitch (Union Carbide, Thornel™)

Table 2. Characteristics of precursors on carbonization

	Carbon yield (Wt%)	Tensile modulus (GPa)
Rayon	20~25	100 1) 390~520 2)
PAN	55~60	150~500
Isotropic pitch	80~85	30~80 1) 400~600 2)
Mesophase pitch	80~85	120~830

1) without hot stretching
2) with hot stretching above 2500°C

MESOPHASE PITCH

Most organic materials can be carbonized on heat treatment at a high temperature above 700-800°C under inert atmosphere. The resulting carbons are classified mainly into the two categories, graphitizable and non-graphitizable carbons. Carbons of the former class exhibit a characteristic of structural conversion on heat treatment above 2000°C, by which the hexagonal carbon-carbon networks are highly oriented in the three-dimensional order. But the latter carbons, non-graphitizable carbons, do not exhibit such a characteristic. Mesophase pitch is known as one of the most typical graphitizable carbonaceous materials. Otani et al. (ref. 4) and Singer (ref. 5) have independently investigated carbon fiber precursors and reported that HPCF with high orientation and crystallinity of graphite can be readily obtained from mesophase pitch.

The processes of mesophase pitch- and PAN-based carbon fibers are shown in Fig. 2. Both processes after the spinning are essentially the same. However, the oxidation in each process has a different purpose. The purpose of the oxidation of mesophase pitch is to cross-link molecules to the extent of making it infusible by introducing oxygen. On the other hand, the oxidation of PAN brings about a ring formation of PAN chain molecules (ref. 6).

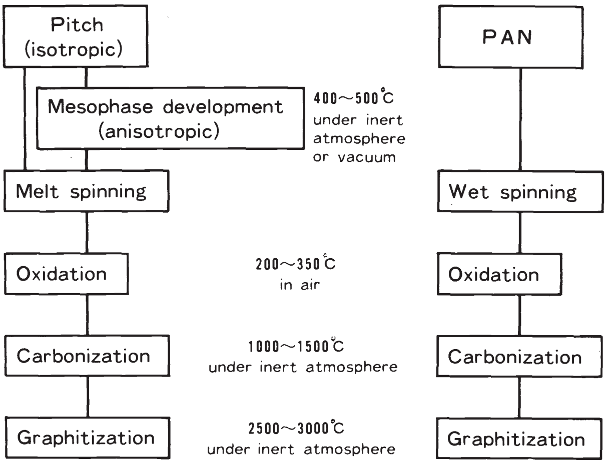


Fig. 2. A comparison of carbon fiber production processes for isotropic pitch, mesophase pitch and PAN.

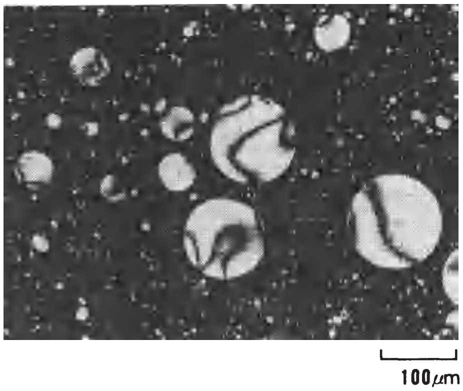


Fig. 3. Mesophase spheres, crossed polarizers.

Pitch is a distillation residue of petroleum or coal tar and is a complex mixture of thousands of aromatic hydrocarbons having a 3-8 fused ring system and an average molecular weight of 300-400. Pitch is first subjected to polymerization and condensation to obtain mesophase. This process is required to convert pitch, an originally isotropic material, to an anisotropic material. Brooks and Taylor (ref. 7) have extensively studied and reported that heat treatment of pitch above 350-400°C results in the formation of spheres of aromatic hydrocarbons (Fig. 3). Further heat treatment facilitates collision and coalescence of the resulting spheres to form mesophase having a large anisotropic domain. Heat treatment of mesophase results in the formation of an anisotropic and infusible solid coke.

Figure 4 shows various stages of the mesophase development during the heat treatment of pitch. The resulting mesophase pitch has a structure in which fused aromatic ring networks are stacked through aromatic π-electron interaction as reported by Brooks and Taylor (ref. 7). Due to this structure, the highly oriented basal plane structure of graphite along the fiber axis can be readily obtained from mesophase pitch by the subsequent carbonization and graphitization. This would be the basis for the higher modulus of mesophase pitch-based carbon fibers compared to PAN-based fibers.

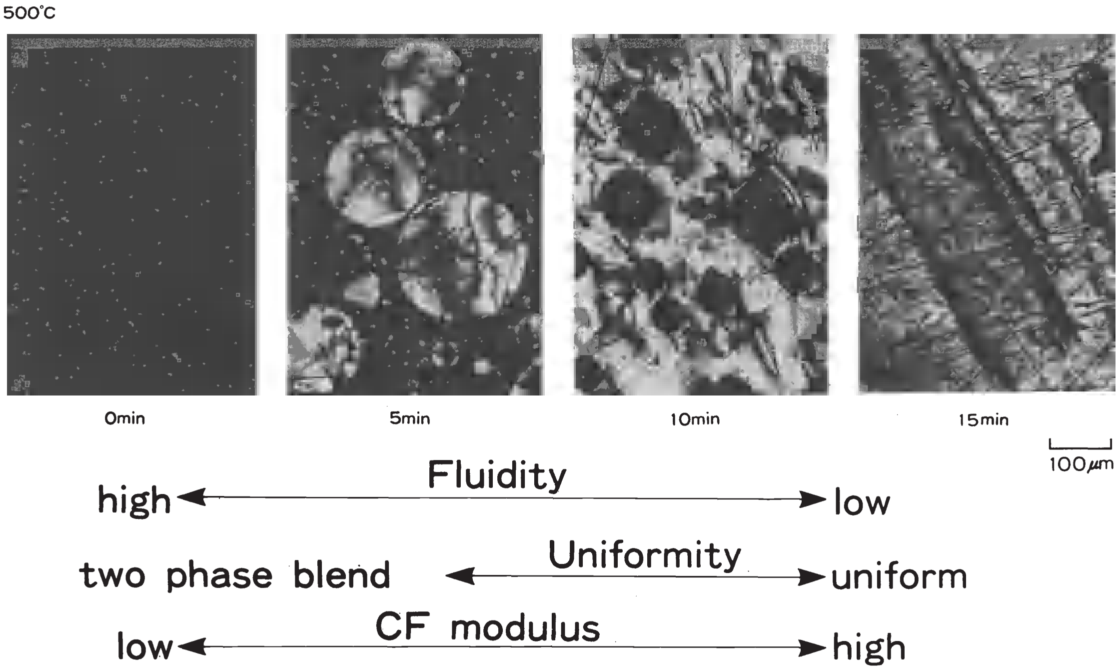


Fig. 4. The development of mesophase from isotropic pitch at 500°C, crossed polarizers.

Polymerization and condensation step is of importance throughout the whole process to obtain such a highly molecular oriented structure of carbon-carbon hexagonal networks. The properties of the mesophase resulting from the polymerization and condensation of crude pitch would determine the spinning characteristics and, consequently, the structure and characteristics of the HPCFs.

The anisotropic domain content of mesophase pitch (mesophase content) depends on the degree of the polymerization and condensation reactions as can be seen in Fig. 4. The mesophase content influences largely the processability of mesophase spinning.

The viscosity difference between an isotropic and an anisotropic regions gives rise to a problem in the spinning of mesophase pitch. When an isotropic content is higher than about 40%, the filament breakage frequently occurs. Therefore from the view point of the spinning stability, the high mesophase content is one of the critical factors to obtain a better processability of melt spinning. Moreover, higher mesophase content is desirable for obtaining the high modulus of carbonized or graphitized fibers as mentioned above. However, a higher mesophase content lowers the fluidity of mesophase pitch because of the higher softening point due to high molecular weight substances in mesophase.

One of the solutions for this problem is to use high spinning temperatures and decrease the melt viscosity of high mesophase containing pitch. But, at such a high temperature, almost all of organic materials including mesophase pitch undergo pyrolysis and produce the gaseous materials which cause filament breakage during spinning.

Another requirement for mesophase pitch is to be free of foreign particles which cause the decrease of the tensile properties of carbon fibers (ref. 8). Such particles contain highly polymerized carbonaceous substances, the so-called "semi-coke", which are insoluble in mesophase pitch. The content of the particle in mesophase pitch is dependent on the degree of polymerization and condensation.

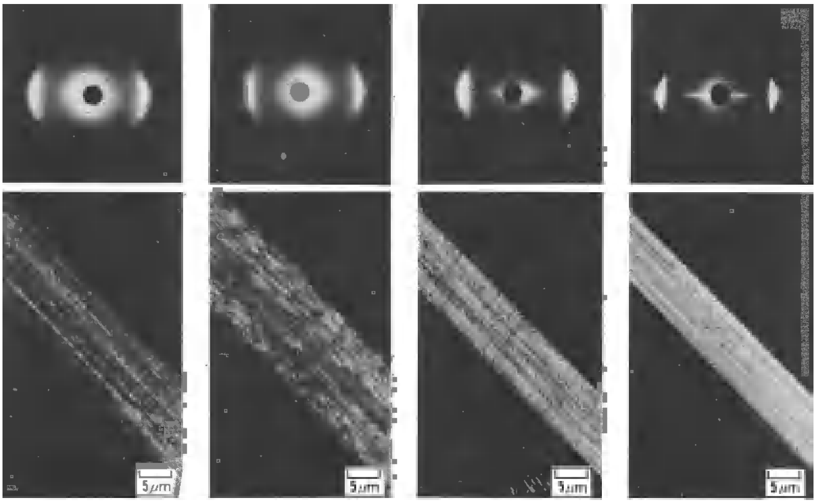
Therefore, it is important to carry out polymerization and condensation effectively (ref. 9, 10) In addition, importance of pretreatment of crude pitch, such as solvent extraction (ref. 11) and hydrogenation (ref. 12, 13), have recently been stressed.

Thus, the desirable properties of mesophase pitch as the precursor of a HPCF with a high quality could be summarized as follows (ref. 14):

1. To have a high content of mesophase and with a large anisotropic domain
2. To exhibit a low viscosity at reasonably low melt-spinning temperatures
3. To be practically free from ash and infusible carbonaceous solids

MESOPHASE PITCH CARBON FIBERS

Mesophase pitch carbon fibers are based on the liquid-crystal characteristics of mesophase pitch. This liquid-crystal pitch can be readily oriented during melt spinning process and can result in highly oriented internal structure of filaments. The changes in the orientation in fibers are shown in Fig. 5. The high orientation in fibers are observed even from the as-spun state both by polarized light microscopy and by X-ray diffraction. The fibers in their as-spun and oxidized state are non-crystalline, however, it is of interest that they exhibit highly oriented X-ray reflections which are similar to the (002) reflection of graphite crystal.



as spun oxidized carbonized graphitized

Fig. 5. Flat-plate X-ray diffraction patterns and crossed polarized micrographs of longitudinal sections of mesophase pitch carbon fibers in the indicated stages.

Figure 6 shows the crystalline size (Lc) and the degree of orientation of oxidized, carbonized and graphitized carbon fibers. Relaxation of the orientation is the largest in oxidized fibers, while the crystalline size is the smallest in carbonized fibers.

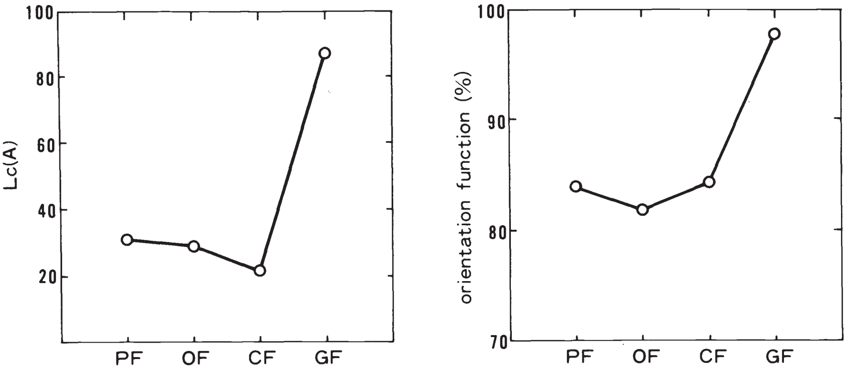


Fig. 6. Crystalline size (Lc) and degree of orientation of each step of mesophase pitch carbon fibers. PF: Pitch fiber (as-spun), OF: Oxidized fiber, CF: Carbonized fiber, GF: Graphitized fiber.

The highly oriented structures of mesophase pitch graphitized fiber are also observed by SEM, while no such large oriented textures is observed for PAN graphitized fiber (Fig. 7). Such highly oriented large graphite structural properties are also observed by transmission electron microscopy (TEM). Figure 8 shows the 002 lattice-fringes of longitudinal sections of PAN and mesophase pitch graphitized fibers. In PAN fiber the stacking of the basal plane of graphite occurs to a lesser extent than mesophase pitch fiber. The non-oriented regions in the mesophase pitch in Fig. 8 are assumed to be non-graphitizable areas, such as isotropic regions, over-polymerized carbonaceous particles and/or oxidized particles, being insoluble in mesophase.

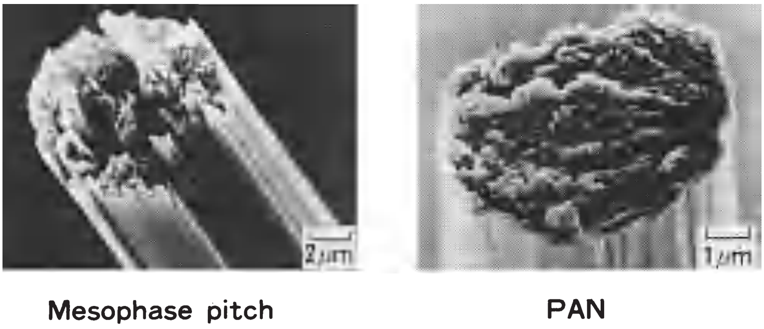


Fig. 7. Fracture surface (SEM) of mesophase pitch and PAN carbon fibers.

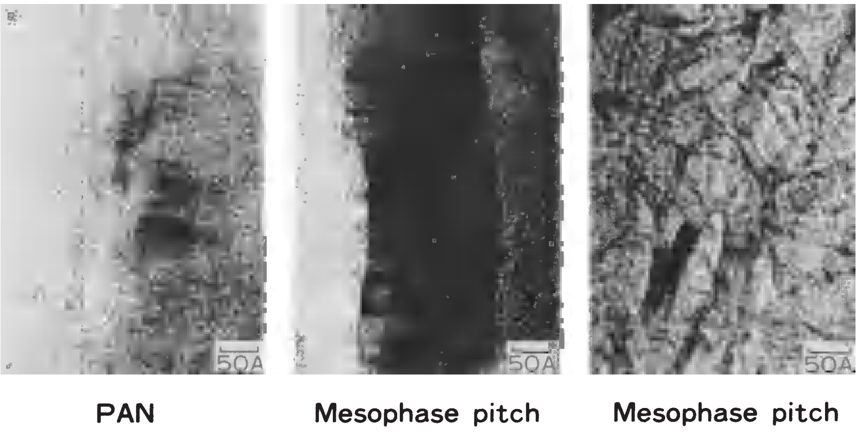


Fig. 8. 002 Lattice-fringes (TEM) of PAN and mesophase pitch graphitized fibers (longitudinal).

The highly oriented graphite structures in mesophase pitch fiber expand for more than 1000Å along the fiber axis as observed by TEM (Fig. 9).

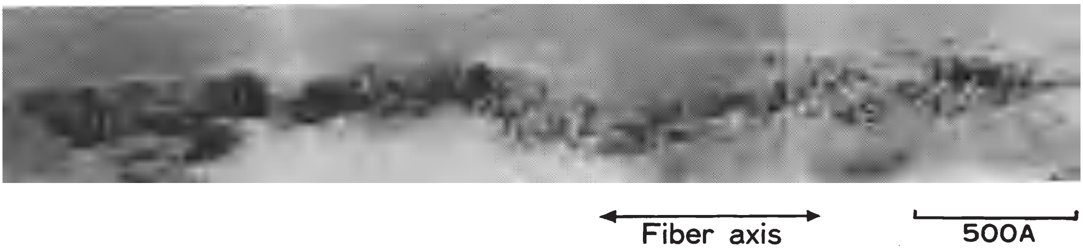


Fig. 9. 002 Lattice-fringes (TEM) of graphitized mesophase pitch fiber along the fiber axis.

The relationship between tensile properties of carbon fiber and its carbonizing temperature is shown in Fig. 10. The tensile strength of mesophase pitch fibers increases with temperature, while PAN shows a maximum strength around 1500°C. The tensile modulus of mesophase pitch fiber (graphitizable) dramatically increases above 2000°C compared with PAN fibers (non-graphitizable).

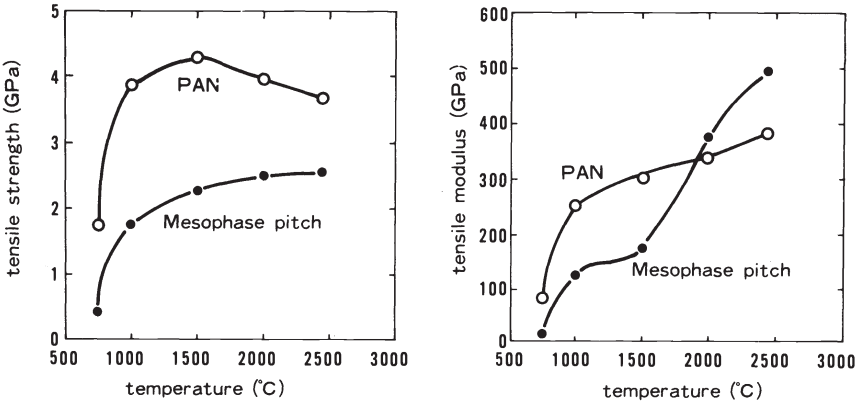


Fig. 10. Relationship between tensile properties of carbon fiber and its carbonizing temperature.

Figure 11 shows the Raman spectral changes during carbonizing and graphitizing process of PAN and mesophase pitch fiber. A typical spectrum reveals two peaks at 1580 and 1360 cm^{-1}. The peak height ratio of 1580 cm^{-1}/1360 cm^{-1} increases on graphitizing in both cases. However, the higher peak height ratio of mesophase pitch is indicative that mesophase pitch is more graphitizable than PAN.

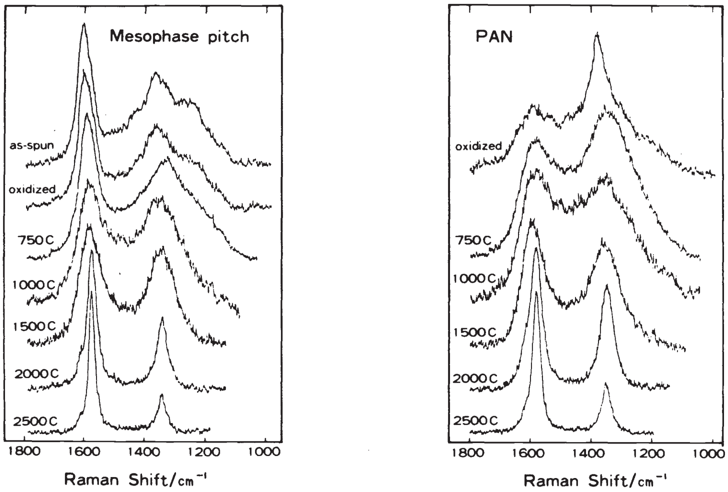


Fig. 11. Raman spectra of carbon fibers.

STRUCTURE OF MESOPHASE PITCH-BASED CARBON FIBERS

Mesophase pitch with suitable properties for melt-spinning can be prepared from hydrogenated coal tar by the process in Fig. 12 (ref. 15). The properties of mesophase pitch thus obtained are shown in Table 3. Figure 13 shows the schematic draw of a melt-spinning apparatus for a single-filament. Mesophase pitch is extruded from the spinneret by pressurized nitrogen and the filament is wound by take-up roll (not shown).

Table 3. Properties of mesophase pitch derived from hydrogenated coal tar.

Softening point	280°C
Glasstransition temperature	225°C
Hydrogen content	3.1wt%
Carbon content	94.5wt%
H/C[1]	0.39
QI[2]	15.8wt%
Anisotropic content	90~95vol%
Mn[3]	560
Mw[3]	650
Mw/Mn[3]	1.2

[1] hydrogen/carbon ratio
[2] quinoline insoluble
[3] quinoline soluble fraction

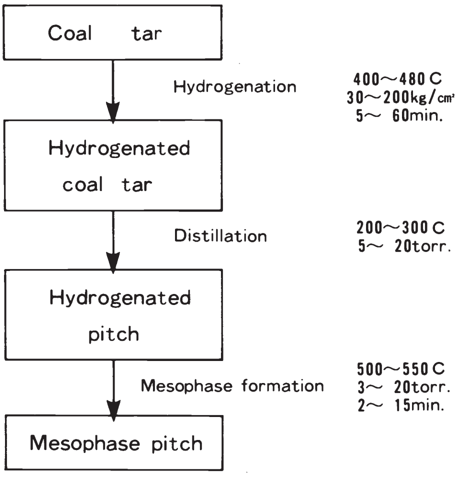


Fig. 12. Pretreatment process of coal tar (ref. 15).

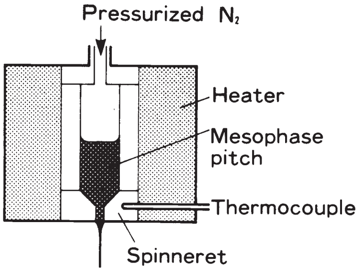


Fig. 13. Schematic draw of the melt-spinning apparatus for a single-filament

The melt-spun fibers are then oxidized, carbonized and, if desired, graphitized. It has been found that a mesophase pitch-based carbon fiber can have one of the several different transverse structures such as radial, "onion-skin", and random structures and intermediate structure of these three (ref. 5). SEMs and polarized micrographs of these three transverse structures are shown in Fig. 14. Radial and onionskin structures are considered to exhibit

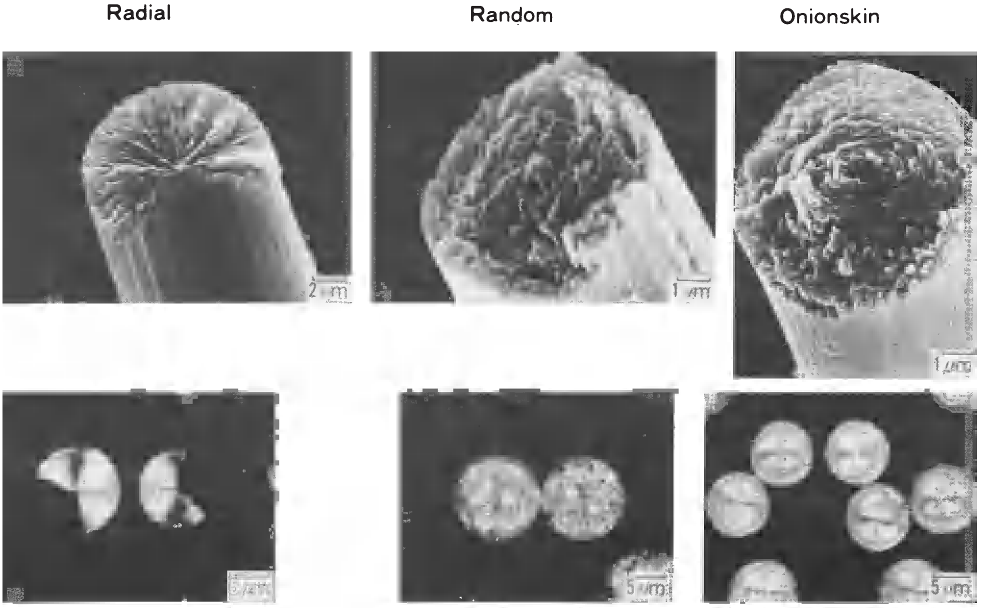

Radial Random Onionskin

Fig. 14. SEMs and crossed polarized micrographs of radial, random and onionskin fibers.

high tensile properties than random one because of the higher orientation. However, cracking along the fiber axis more readily occurs during oxidation and carbonization in the case of carbon fiber with a radial structure than those with the others. Such cracks affect as the defects on the fiber surface and decrease the tensile properties. On the other hand, the graphite whisker which is crystallized from vaporized carbon in arc electrodes is found to have a circumferential structure and has attained the tensile strength of 20 GPa (ref. 16). For this reason, onionskin structure is also expected to exhibit high tensile properties.

Despite the recognition about the importance of controlling the internal structure of mesophase pitch carbon fibers, there has been no effective method in a practical sense. We have found that transverse structure of mesophase pitch-based carbon fibers depends on the shear in spinneret and the dimension of die used for the melt-spinning procedure (ref. 17). Figure 15 shows the effect of shear in a spinneret on the high orientation of mesophase along the fiber axis. Figure 16 shows the experimental results of the effects of shear in the spinneret on the internal structure of carbon fibers.

Viscoelastic parameters in a cylindrical plug flow are defined by Hagen-Poiseuille equation (1).

$$\Delta P = 128\eta \; LQ/\pi D^4 \qquad (1)$$

where ΔP is the pressure difference between both ends of the cylinder, η is an apparent vicosity L is the length of the cylinder, Q is the volume fraction and D is the diameter of the cylinder (Fig. 17). The magnitude of the orientation is considered to be increased with the increase in the shear stress (τ) and the mean resident time in the cylinder (t). These two parameters,

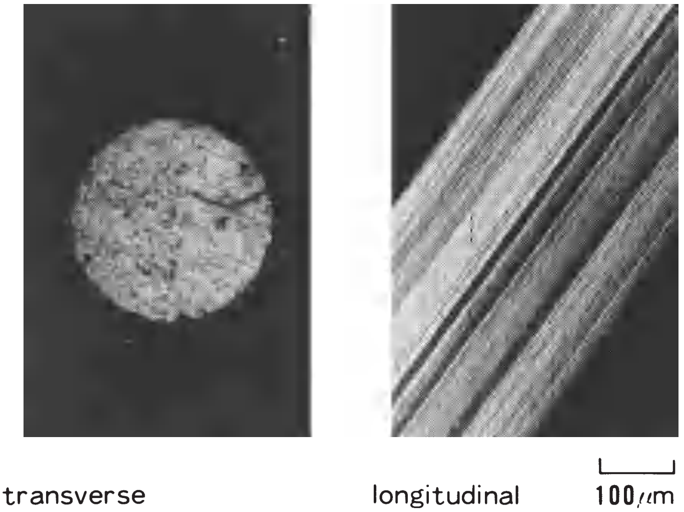


Fig. 15. Mesophase pitch extruded from spinneret, crossed polarizer.

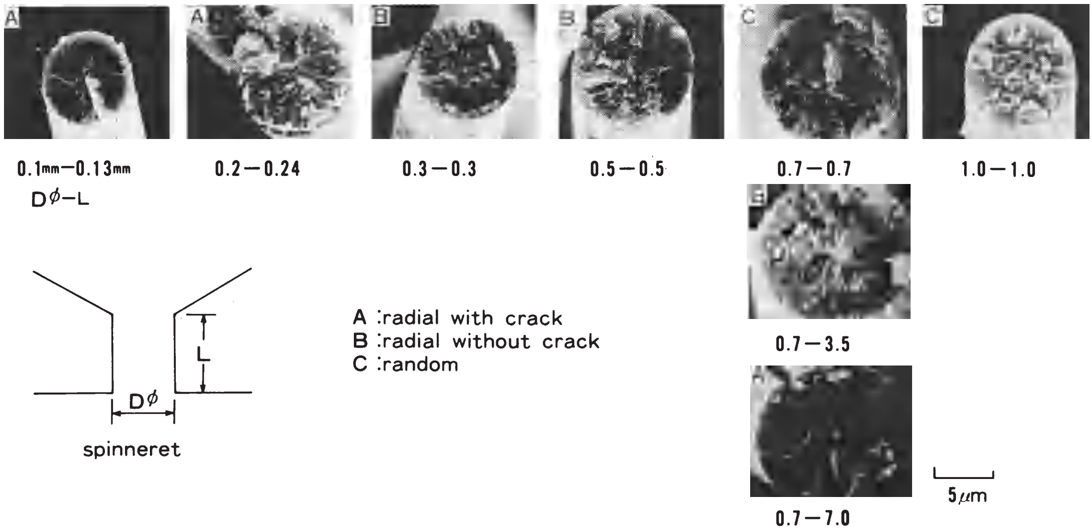


Fig. 16. Effects of shear in the spinneret on the internal structure of carbon fibers. D: Diameter L: Length of the die (mm)

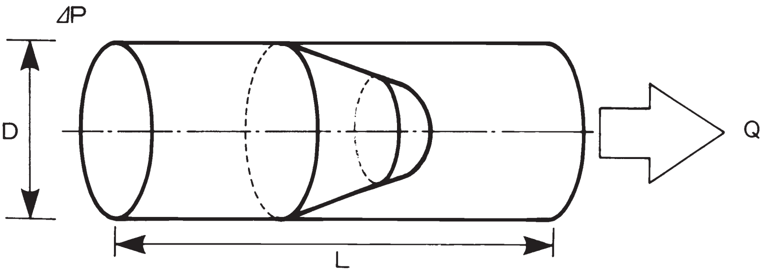


Fig. 17. Schematic diagram of cylindrical flow.

τ and t, can be expressed by the following equations 2 and 3, respectively, using the parameters used in the Hagen-Poiseuille equation 1.

$$\tau = 32\eta\, Q/\pi D^3 \qquad (2)$$

$$t = \pi D^2 L/4Q \qquad (3)$$

From the equation 3, t is a function of L under the conditions where the diameter of the spinneret (D) and the volume fraction (Q) are constant. Under such conditions, as shown in Fig. 16 (D = 0.7 mm, L = 0.7-7.0 mm), the internal structure of the resulting fiber was varied from a random, a radial, and a radial with crack type, depending on the length of the spinneret (L). The greater value of L seems to be preferable to obtain a radial internal structure. However, when L value is too large, cracking along the fiber axis occurs. Therefore, in a practical sense, it is important to optimize the length of the spinneret to obtain a desired internal structure.

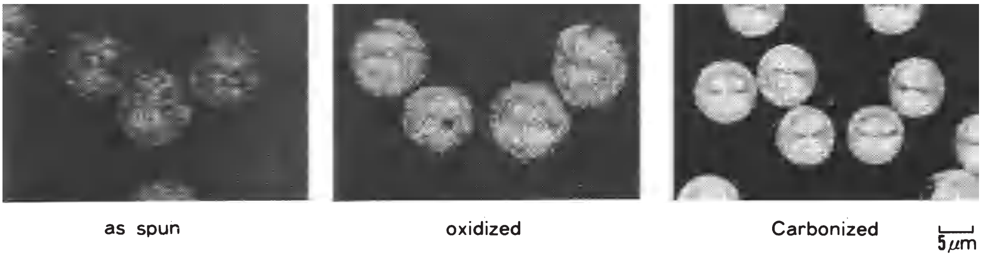
These results also indicate that the degree of shear is an important factor to determine the internal structure since the degree of shear is considered to be a function of t. Now, the equation 4 is derived from the equation 3.

$$t = (\pi D^3/4Q)\,(L/D) \qquad (4)$$

From the equation 4, t is also a function of the diameter of the spinneret (D) and a radial type of internal structure is expected to be preferentially obtained using a spinneret with a larger diameter (D) under the conditions where L/D and Q are constant. However, as shown in Fig. 16 (D=0.3-1.0 mm) the smaller value of D was preferable to obtain a radial type of internal structure. Furthermore, a radial with crack type carbon fiber is obtained when the smaller D (even with the larger L/D) is employed (Fig 16, D=0.1-0.2 mm). Since the degree of shear is also considered to be dependent on τ of equation 2 and τ is a function of D, these results suggest that the shear stress (τ) is more important factor than the mean resident time (t) in determining the internal structure of the resulting carbon fiber.

Carbonized fiber

Spinneret



as spun

oxidized

Carbonized

Fig. 18. SEM and crossed polarized micrographs of onionskin carbon fiber and the shape of the spinneret.

Yamada et al. (ref. 18) have reported that the internal structure of carbon fiber varies from onionskin to random or onion-surface radial-core, then to radial and finally to radial with crack as the spinning temperature decreases. Their observations that a random type internal structure was preferentially produced by spinning at a higher temperature and that a radial type was produced at a lower temperature, can be explained, at least partially, by the equation 2 since at a lower temperature, η is greater which means τ is greater and, thus, the degree of shear is greater.
Their method to obtain onionskin structure requires a high temperature spinning and often results in the formation of voids in fibers due to the pyrolytic gaseous materials.
To avoid the pyrolysis, a relatively low spinning temperature should be employed. To meet this requirement, we have investigated the effects of the flow of mesophase in the spinneret and established a new spinning technology to obtain onionskin structure fibers by expanding the size of flow in the spinneret. Figure 18 shows the internal structures of the onionskin fibers obtained by our method and the shape of the spinneret used. From polarized microscopic observation using sensitive color plate, radial and onionskin structure of mesophase pitch as spun fibers can be easily distinguished by the interference colors. Using this technique, radial and onionskin structures in the cross section of as spun fibers obtained by our method were demonstrated and these internal structures were found to be preserved even in carbonized and graphitized fibers.

In conclusion, the internal structure of mesophase pitch carbon fibers is drastically affected by the spinning conditions, especially the factors determining the flow of mesophase in the spinneret, namely the diameter, the length, and the shape of the spinneret. Mechanisms by which these factors determine the internal structure of the resulting carbon fiber remain unclear. More detailed investigations on mesophase behavior in the cylindrical flow, especially on the orientational phenomena under shear, are needed.

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