Transverse Sphere and Texture of Carbon Fibers Prepared through Cross Shaped Nozzles of Different Lobe Dimensions

Korai, Yozo
Institute of Advanced Material Study Kyushu University

Oka, Hidetoshi
Institute of Advanced Material Study Kyushu University

Hong, Seong-Hwa
Institute of Advanced Material Study Kyushu University

Mochida, Isao
Institute of Advanced Material Study Kyushu University

他

https://doi.org/10.15017/7904

出版情報：九州大学機能物質科学研究所報告. 13 (1), pp.7-11, 1999-07-08. 九州大学機能物質科学研究所
バージョン：
権利関係：

Transverse Sphere and Texture of Carbon Fibers Prepared through Cross Shaped Nozzles of Different Lobe Dimensions

Yozo KORAI[*1], Hodetoshi OKA[*1], Seong-Hwa HONG[*1], Isao MOCHIDA[*1], and Isamu KATO[*2]

Methylnaphthalene derived mesophase pitch was spun through Y- and cross- shaped nozzles of different lobe dimensions in temperature range of 280 to 295°C by fixing the spinning rate to evaluate die-swelling phenomena which deformed cross-sectional shape and domain alignment of the carbon fiber. The higher temperature of spinning enhanced the deformation through the lower viscosity. The thinner lobe emphasized the die-swelling through the larger shear rate, which reduces the viscosity, although the nozzles of the present study had the same cross-sectional area. Shape factors of the nozzle and fiber describe the extents of cause and results of die-swelling, respectively. Die-swelling is found to change the radial type alignment of the constituent domains to random order. The degrees of preferred orientation along the fiber axis were slightly influenced by die-swelling. The pressure in spinning and the nozzle shape were correlated to the deformation extent of the resultant fiber.

Introduction

Super performances of mesophase pitch based carbon fibers have been pursued in terms of their tensile strength, compressive strength, and thermal conductivity[1)~3)]. Control of their microtexture and shape is assumed as a key to achieve such performances. In previous studies, present authors found the micro-structure depended mainly on the properties of the mesophase pitch and spinning conditions[4),5)]. Spinning through the nozzle deforms the micro assembles of the mesogen molecules in the mesophase pitch to be aligned along the nozzle wall. Once the alignment is determined in spinning, the microstructure seldom changes in the stabilized and carbonized steps.

The transverse texture of carbon fiber is typically classified into radial, random, and onion alignment, depending on the spinning conditions[6)]. Fibers, which have linear-radial alignment, form the wedges during the heat-treatment process, which causes decrease in tensile and compressive strength[7)]. Generally, fibers with random alignments have better compressive strength because the micro domains shrink equally at the heat-treatment[8)]. Such an alignment is formed through the relaxation at the outlet of the nozzle and the surface tension while the mesophase is deformable. The former relaxation phenomena is called die-swelling to lead to a expanded diameter of the fiber which is pulled down to be solidified in a thinner fiber[9)]. The extent of die-swelling is believed to be governed by the extent of tension along a stream line accumulated in the fiber while the pitch runs in the spinneret, and its release in comparison with the solidification rate at the outlet of the spinneret. Hence, the viscosity of mesogen assemble in the mesophase pitch, surface tension, spinning conditions such as shape and dimension of spinneret, temperature and shear stress, and wind up rate may influence the extent of deformation. Thus, the transverse shape and micro texture of the resultant carbon fiber are controlled by the balance of alignment forced in the nozzle and its relaxation.

In the present study, transverse shape and texture of the mesophase pitch based carbon fibers were studied by spinning the mesophase pitch derived from methylnaphthalene (mNP) through cross-shaped nozzles of different lobe dimensions at several temperatures to control them at the spinning. The spinning rate was constant for both spinnerets by changing the pressure. The viscosity of the mesophase pitch during spinning is determined by the temperature and pressure and the die-swelling being expected to vary its extents.

Experimental

Sample

Table 1 summarizes some properties of mesophase pitch used in this study. The mesophase pitch was prepared from methylnaphthalene with HF/BF_3 as a catalyst by Mitsubishi Gas Co. The mesophase pitch has 100vol% anisotropy at room temperature.

Received May 13, 1999

*1. Institute of Advanced Material Study, Kyushu University.
*2. Central Research Institute, Nissekimitsubishi Oil Co.

Table 1	Some properties of methylnaphthalene mesophase pitch									
	SP	AC	Solubility(wt%)						X-ray parameters	
Code	(°C)	(vol%)	BS	BI-PS	PI	H/C	fa		d002(nm)	Lc002(nm)
mNP	205	100	52	19	33	0.69	0.81		0.3524	7.5

SP: softening point, AC: anisotropic content

Spinning

This mesophase pitch was heated at a heating rate of 7°C/min to 275°C under nitrogen flow and spun into fibrous through two cross-shaped spinning capillaries at a temperature range from 275°C to 290°C, using laboratory scale mono-filament apparatus. Shape and size of spinnerets were illustrated in Fig. 1, and defined as +-0.0886 and +-0.119, respectively. The depth of the spinneret was 0.9mm. Both spinnerets had the same cross-sectional areas.

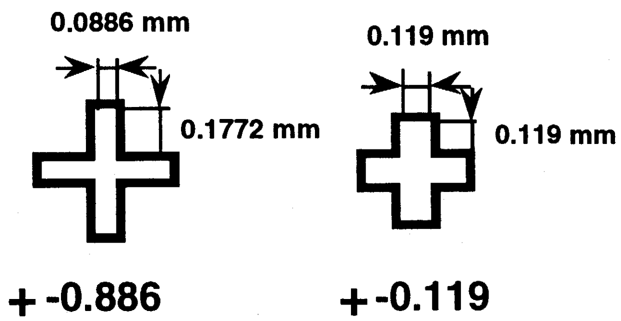

Fig. 1. Some properties of methylnaphthalene mesophase pitch

The rate of extrusion from the spinning nozzle was fixed at 60 mg/min by controlling pressure adjustable to the temperature and capillary dimension. The extruded mesophase pitch was wound up at a speed of 300 m/min.

Stabilization and Carbonization

The prepared pitch fibers were oxidatively stabilized at 270°C for 30min. Heating rate was fixed at 0.5°C/min and carbonized at 1000°C for 1h at a heating rate of 10°C/min in argon atmosphere. The carbonized fibers were cut by the ceramic scissors in liquid nitrogen to observe cross sectional area. The transverse textures of the carbonized fibers were observed by a scanning electron microscope (JEOL JSM-5400). The preferred orientation was calculated from the orientation angle measured by a X-ray diffractometer (RIGAKU RAD-B).

Results

Fig. 2 shows the torque pressure needed to extrude the pitch by 60mg/min at each spinning temperature through the various spinning spinnerets. Higher temperature lowered the pressure for the extrusion. Figs. 3 and 4 showed the transverse shapes and textures of carbonized fibers spun through the nozzles of different lobe dimensions. At lower temperature of 275°C, cross-shaped fibers were obtained through both nozzles, although the edges of the lobe were rather round. Higher spinning temperature deformed the cross-shape into rectangular shape by reducing the curvature between lobes. Such deformations appear to occur at lower temperature through the nozzle lobes of smaller dimension. The line-origin radial alignment was observed in the fibers spun at lower temperatures. The higher temperatures modified the alignment into random along with the deformation of the transverse shape. The thinner lobe tended to deform more extensively the shape of the fiber and to give more random trend in the transverse alignment.

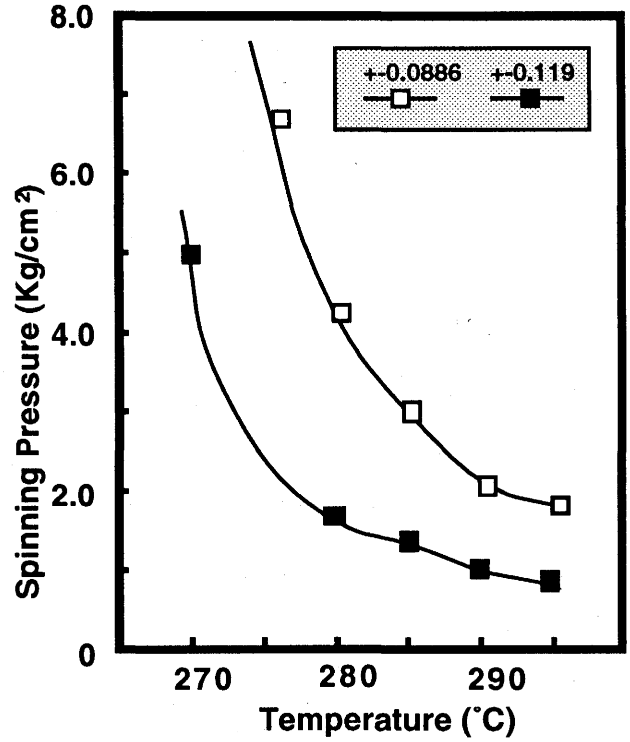

Fig. 2. Torque pressure needed to extrude the pitchthrough the spinnerets at a rate of 60 mg/min

Fig. 5 illustrates the degrees of preferred orientation of the as-spun fibers through the nozzles of different lobe dimensions. The degree of orientation increased along the spinning temperature up to 290°C, where the highest degree was achieved regardless of the lobe dimensions. Further higher temperature of spinning slightly reduced the orientation degree. The lobe dimension influenced slightly the degree of orientations although some differences were observable at lower spinning temperatures.

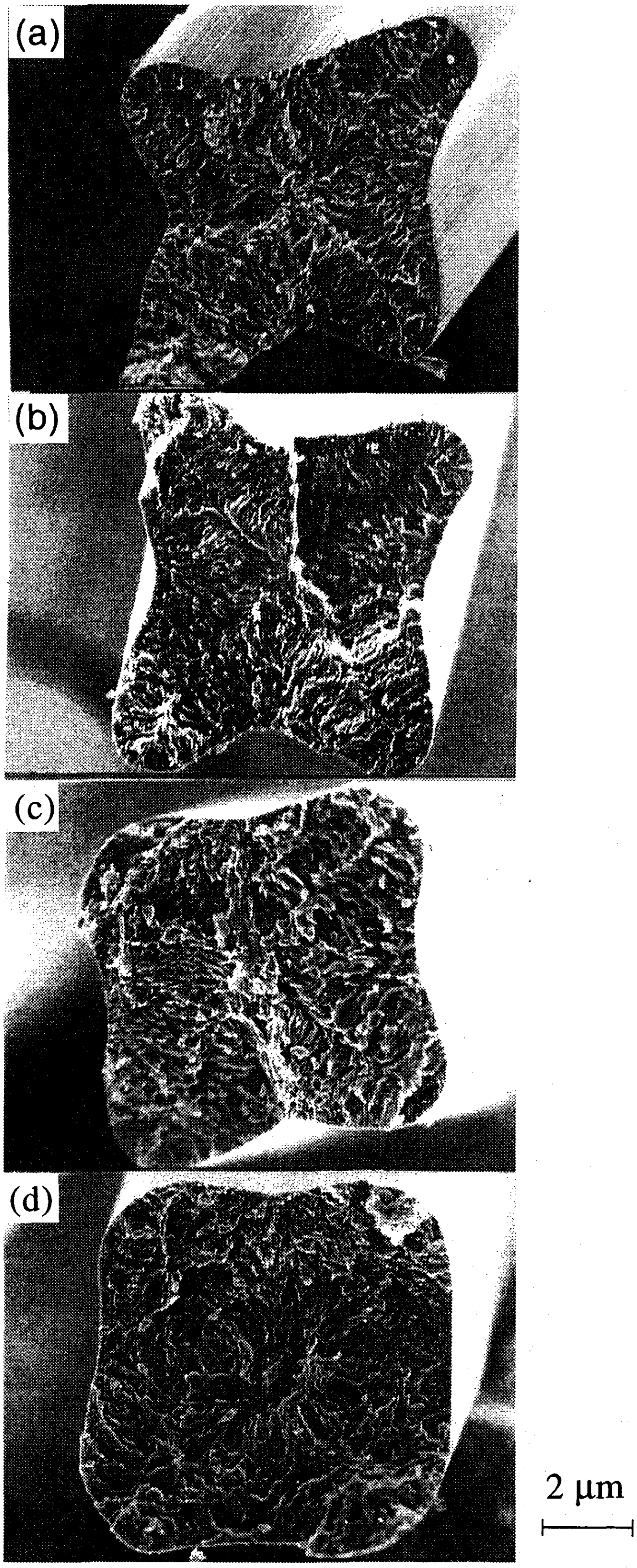

Fig. 3. Transverse shape and texture of caron fiber spun through +-shaped nozzles with thick lobe (+-0.199). spinning temperature: (a) (a) 275 °C, (b) 280°C, (c) 285°C, (d) 290°C

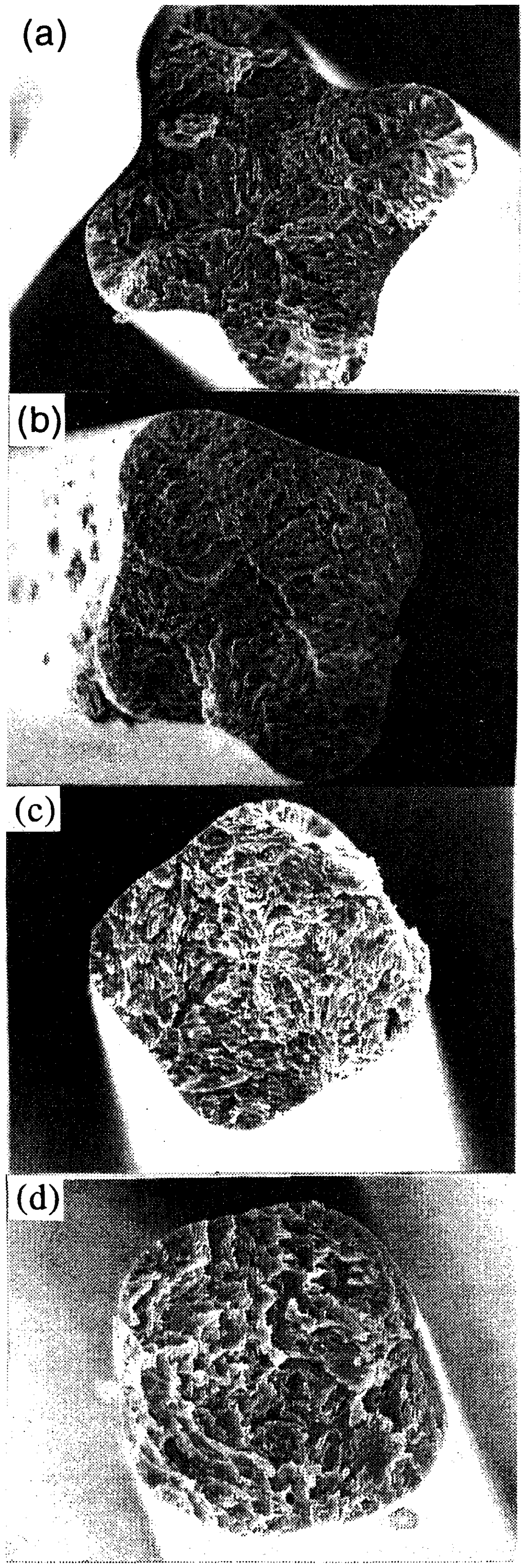

Fig.4. Transverse shape and texture of carbon fiber spun through + - shaped nozzles with thin lobe (+ -0.0886). spinning temperature: (a) 275 °C, (b) 280°C, (c) 285°C, (d) 290°C

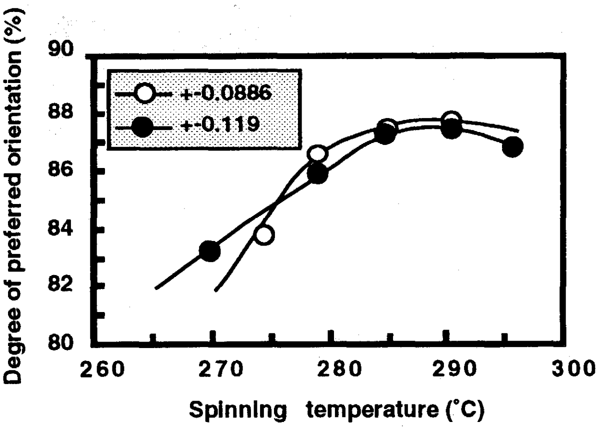

Fig. 5. Degree of preferred orientation of pitch fibers spun with +-0.0886 and +-0.119 nozzles

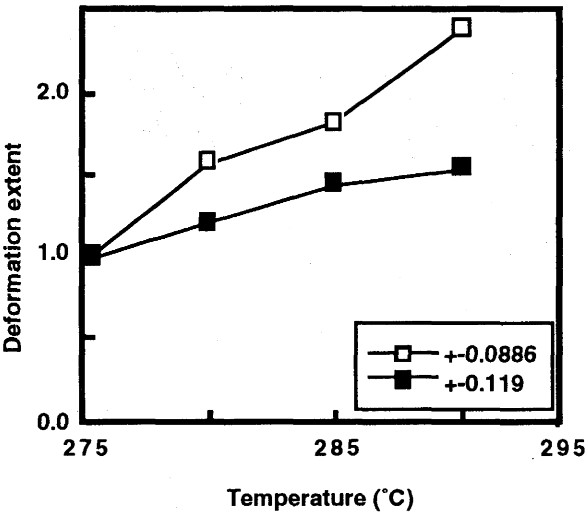

Fig. 7. The correlation between spinning temperature and deformation extent

Discussion

The present study revealed that the transverse shape and texture of the carbon fiber were controllable through the dimension of the spinneret as well as the spinning temperature. The deformation extent of the fiber is described by the shape factors defined by the ratios of width and length of the lobe (W/L) in the cross-sectional surface as illustrated in Fig. 6, where the ratio of the fiber spun at 275°C was defined 1. Fig. 7 illustrates the correlation between the spinning temperature and the extent of deformation. The deformation increased with the spinning temperature. W/L ratio through the thinner lobe dimension changed their ratio greatly.

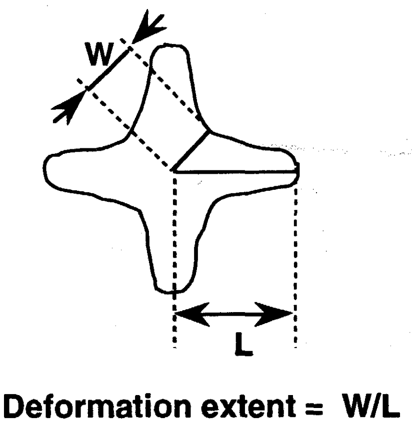

Fig. 6. Definition of deformation extent in the resultant carbon fiber

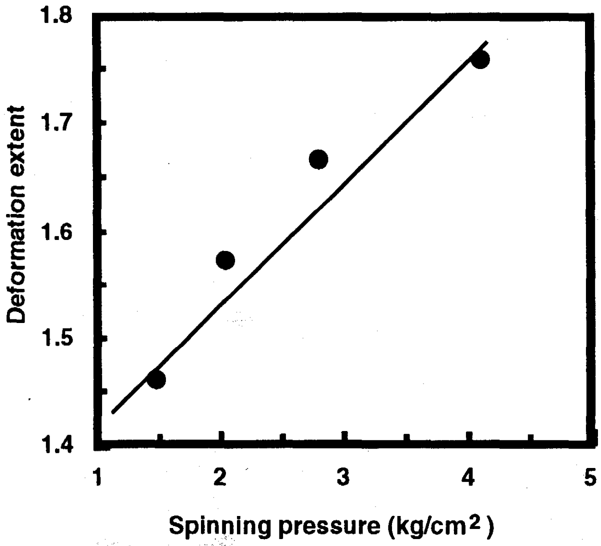

Fig. 8. The correlation between deformation extent and spinning pressure (spun at 285°C)

Fig. 8 showed the correlation between the deformation extent and spinning pressure. This figure indicates that the higher spinning pressure make the deformation extent large. This may be ascribed to the result from the flow properties of mNP. In the spinning temperature range, mNP showed non-Newtonian flow where the viscosity changes very sharply with the shear stress[10), 11)].

Such changes of the transverse shape and texture are ascribed to a kind of die-swell (Barus effect) and surface tension of the molten pitch fiber. The former occurs at the outlet of the spinneret by the liberation of the shear stress accumulated in the fiber surface by the forced alignment in the spinneret. Such effect is more emphasized in the thinner lobe dimension of larger wall area.

The assembles of planar mesogen molecules in their domains in the mesophase pitch pass through the nozzle to be deformed, aligned, and packed densely along with the fiber axis. The liberation of such stress allows the domains to swell. Then the swelled pitch deforms to minimize the surface energy of the fiber at the surface by reducing the curvature of cross-shape to be square. Hence, the deformation of the fiber causes both the die-swell and the surface tension.

Thus, the extent of the deformation is found to be governed basically by the viscosity of the pitch at the outlet of the spinneret. The transverse texture of the fiber shifted radial to random as the spinning temperature increases. This result indicates that the alignment of the micro domain was disordered when the mesophase pitch swelled at the outlet of the nozzle. Such die-swelling hardly influences the orientation along the fiber axis up to spinning temperature of 290°C, which slightly decreases above this temperature. Such decrease may reflect that the mesogen molecules in the mesophase pitch re-align at the outlet of the nozzle. It is of value to point out that the preferred orientation is not strongly influenced by the die swell.

The transverse texture and shape of the carbon fiber are controllable without reducing the preferred orientation of the graphitized fiber. It is strongly expected that carbon fiber of higher compressive strength can be produced without reducing the tensile strength and modulus.

Acknowledgment

This research was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research on Priority Areas (Carbon Alloys), 09243101, 1997 and Grant-in-Aid for Scientific Research (C), 09650941, 1997.

References

1. Edie, D. D., Fox, N. K. and Barnett, B. C., Carbon, 1986, **24**, 481.
2. Korai, Y., Nakamura, M., Mochida, I., Sakai, Y. and Fujiyama, S., Carbon, 1991, **29**, 561.
3. Otani, S., Okubo, K. and Matsuda, S., "Carbon Fiber", Kindai Henshusya, Tokyo, 1983, 644.
4. Mochida, I., Yoon, S. H. and Korai, Y., Carbon, 1994, **32**, 1182.
5. Mochida, I., Fortin, F., Yoon, S. H. and Korai, Y., Carbon, 1990, **32**, 1119.
6. Yamada, Y., Matsumoto, S., Fukuda, K. and Honda, H., TANSO, 1981, **107**, 144.
7. Matsumoto, T., Pure Appl. Chem., 1985, **57**, 1553.
8. Mochida, I., Yoon, S.H., Fortin, F. and Korai, Y., Extended abstracts Carbon 94, Granada, Spain, 1994, 683.
9. Mochida, I., Yoon, S. H., and Korai, Y., J. Mater. Sci., 1993, **28**, 2331.
10. Mochida, I., Yoon, S.H., Korai, Y. and Kato, I., Carbon, 1994, **32**, 273.
11. Han C. D. and Park, J. Y., J. Applied Polymer Sci., 1973, **17**, 187.