BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3710—3714 (1972)

High Modulus Carbon Fibers from Pitch Materials[1]

Sugio Ōtani, Shoji Watanabe, Hosaku Ogino, Kazuo Iijima, and Teruyo Koitabashi
Faculty of Technology, Gunma University, Kiryu, Gunma

(Received July 15, 1971)

Preparation of high modulus carbon fibers from pitch materials was attempted by two methods, stretch-graphitization and the use of a special pitch material composed of highly oriented constituent molecules. It was shown that carbon fiber of high tensile strength and of high modulus can be prepared by stretch-graphitization, and high modulus carbon fiber by heat treatment without stress from the pitch of tetrabenzophenazine. The property of precursor was found to have an important effect on the structure of the fiber.

Studies on the preparation and structure of high modulus carbon fibers have shown that they exhibit a high degree of preferred orientation of the constituent layer planes[2,3] and heat treatment under stress

---

[1] This work was presented at the Meeting of the Chemical Society of Japan held in Tokyo, April 2 (1971) Preprint No. 5248, p. 1018.

[2] J. W. Johnson and W. Watt, *Nature*, **215**, 385 (1968).

[3] A. Fourdeux, R. Perret, and W. Ruland, International Conference on Carbon Fiber, their Composites and Applications, London, Preprint No. 9 (1971).

is essential for successful preparation.[4,5] Most of these investigations have dealt with PAN(polyacrylonitrile) or rayon precursors. Until 1968, pitch precursor had not been thought to be very suitable material for high modulus carbon fiber.[6] Since then some works[7–11] were reported on the preparation of high modulus carbon fiber from pitch precursor by stretch-graphitization. The results, however, were not so satisfactory as those for rayon or PAN precursors. We found that two kinds of pitch based carbon fibers of which mechanical properties are almost equal to PAN based high modulus or high strength carbon fibers could be prepared by stretch-graphitization using a larger stress and a higher temperature than in the preliminary works.[7–9]

During the course of investigation on carbonization of synthetic aromatic compounds, it was found that tetrabenzo(a,c,h,j)phenazine was converted by heating into a pitch-like material which had a high degree of preferred orientation of the constituent molecules. By use of this material, carbon fiber having a high degree of preferred orientation of constituent layer planes was prepared without stretch-graphitization.

This paper describes improved results obtained by stretch-graphitization method and the evaluation of new method.

Experimental

Carbon Fibers Prepared by Heat Treatment under Stress. Original carbon fibers was two kinds of commercial pitch based carbon fibers with the different purches time. Both fibers with diameters 8—12 μ, named (M) and (S) respectively, were prepared at 1000°C by the Kureha process.[12] No distinct difference was observed in their mechanical properties, X-ray diffraction profiles or densities.

Preparation. Improvement of the design of the furnace gave rise to successful application of higher temperature and greater stress than those in previous work.[7–9] The bundles (2000—3000 deniers) of the original carbon fibers were suspended along the central axis of graphite tube heater. A load (0.5—1.0 g per denier) was attached to the end of the bundle. The bundles were then heated in nitrogen atmosphere from room temperature up to 2800°C at a rate of 270±20°C per minute and then immediately cooled. There was a gradient of temperature along the fiber axis in the tube heater and the homogeneous region at maximum temperature was about 4 cm in length. A change in length of the carbon fibers was clearly observed at temperatures above 1800°C. The amount of change increased with the increase of applied stress.

Mechanical Properties. The preferred orientation of the basal planes in the fibers remarkably increased by the plastic deformation during the course of heating under stress. The diameter of the resulting fibers was 4—7 μ. Their tensile strength was closely related with their orientation parameters as shown in Fig. 1. The orientation parameters are represented by the definition of Brydges and Badami.[13] Mechanical properties were measured with a Tensilon using a cross-head speed of 2 mm/min and 2 cm guage length. The average values were calculated from 30—50 runs. The values of typical PAN based carbon fibers, Royal Aircraft Establishment(RAE) carbon fiber Type I (high modulus type) and Type II (high strength type), measured under the same conditions, are also plotted as control. We see that both pitch based carbon fibers have the same trend as regards relationship between tensile strength and orientation parameter. However, samples from the carbon fiber (M) generally have a higher Young's modulus at a given tensile strength than other samples (Fig. 2). The carbon fiber with the highest modulus (G–1) has one of about 49 × 10^2 ton/cm^2. That with the highest tensile strength (G–2) and prepared from carbon fiber (S) has a strength of about 29 ton/cm^2. G–1 might be said to be a high modulus carbon fiber and G–2 a high strength carbon fiber. Other properties of G–1 and G–2 are listed in Table 1.

Carbon Fiber from Highly Oriented Pitch Materials. It is well-known[14,15] that a number of anisotropic spherules are formed in amorphous molten pitch materials by heating at 350—400°C. They grow with rising temperature and/or extending heating period. The mesophase anisotropic spherules are composed of highly oriented polycyclic aromatic plane molecules. Thus the pitch materials heated at 400—500°C generally consist of anisotropic spherules

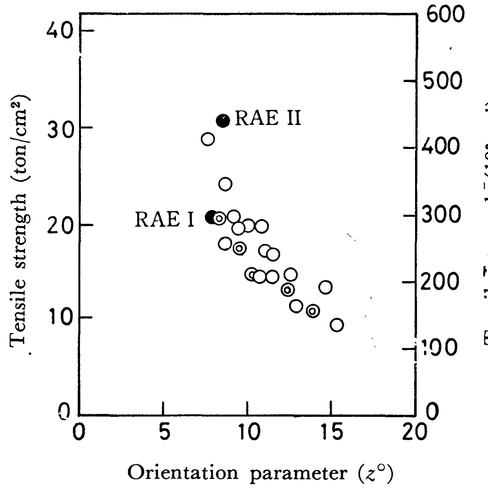

Fig. 1. Tensile strength of the fibers as a function of the orientation parameter.
○ Samples from carbon fiber (S)
◎ Samples from carbon fiber (M)
RAE I: RAE carbon fiber Type I (as control)
RAE II: RAE carbon fiber Type II (as control)

---

[4] J. W. Johnson, J. R. Marjoran, and P. G. Rose, *Nature*, **221**, 357 (1969).

[5] R. Bacon and W. A. Schalamon, Eighth Conference on Carbon, Abstract, Paper No. 58; *Carbon*, **6**, 199 (1968).

[6] S. Otani, A. Yokoyama, and A. Nukui. A. C. S. 156th National Meeting, Atlatic City, N. J. (Sept. 1968), Preprint p. 1385. Applied Polymer Symposia No. 9, 325 (1969).

[7] S. Otani, Y. Kokubo, and T. Koitabashi, 22th Meeting on Carbon Materials, Tokyo, (Dec. 1969), Preprint p. 5.

[8] S. Otani, Y. Kokubo, and T. Koitabashi, This Bulletin, **43**, 3291 (1970).

[9] S. Otani and S. Watanabe, 9th Conference on Carbon at Boston, (June, 1969), Summary of Paper, 29.

[10] H. Hawthorne, C. Baker, R. H. Bentall, and K. R. Linger, *Nature*, **227**, 946 (1970).

[11] H. Hawthorne, International Conference on Carbon Fibers, their Composites and Application, at London, (1971), Preprint Paper No. 13.

[12] T. Araki and S. Gomi, Applied Polymer Symposia, No. 9, 331 (1969).

[13] W. T. Brydges, D. V. Badami, J. C. Joiner, and G. A. Jones, Appllied Polymer Symposia No. 9, 255 (1969).

[14] J. D. Brooks and G. H. Taylor, *Carbon*, **3**, 185 (1965).

[15] H. Honda, H. Kimura, Y. Sanada, S. Sugawara, and T. Furuta, *ibid.*, **8** 181 (1970).

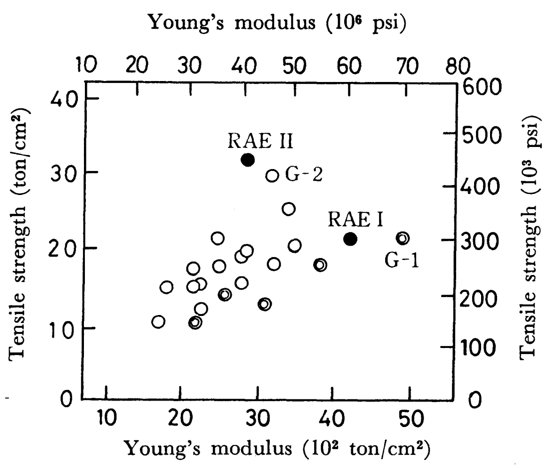

Fig. 2. Mechanical properties of the stretch-graphitized carbon fibers.
○: Samples from carbon fiber (S)
◎: Samples from carbon fiber (M)
RAE I: RAE carbon fiber Type I (as control)
RAE II: RAE carbon fiber Type II (as control)

and amorphous parts.

Tetrabenzo(a,c,h,j)phenazine ($C_{28}H_{16}N_2$) was converted into a pitch-like material by heating, which was optically anisotropic over the whole body (PZ pitch). It can thus be regarded as a typical highly oriented pitch material.

Preparation of Tetrabenzo(a,c,h,j)phenazine. Tetrabenzo(a,c,h,j)phenazine was synthesized from diaminophenanthrene chlorohydrate and phenanthraquinone according to Schmidt and Söll.[16] The crystal purified by recrystallization from nitrobenzene solution is denoted by PZ-1. Since recrystallization was rather cumbersome, an attempt was made to omit final purification treatment by use of both raw materials purified before synthesis. The crystal thus prepared is denoted by PZ-2, which is essentially the same as PZ-1 except for the presence of about 1% of oxygen, appearance of a very weak absorption band around 1700 cm^{-1} in infrared spectrum and a low melting point of 462°C.

Conversion of Pitch Material from PZ Crystals. PZ-1 was fused into a yellowish brown liquid at 480°C and was converted gradually into a pitch-like material above 550°C and into a coke at 600°C. When PZ-1 was heated in a glass tube under nitrogen, the yields of the coke at 600°C and of PZ recrystallized through vapor phase in the cold part of the tube were respectively 65 and 33 wt%, gaseous product being about only 1 wt%. The spinnable pitch material was formed from PZ-1 by heating at 580°C for 60 min.

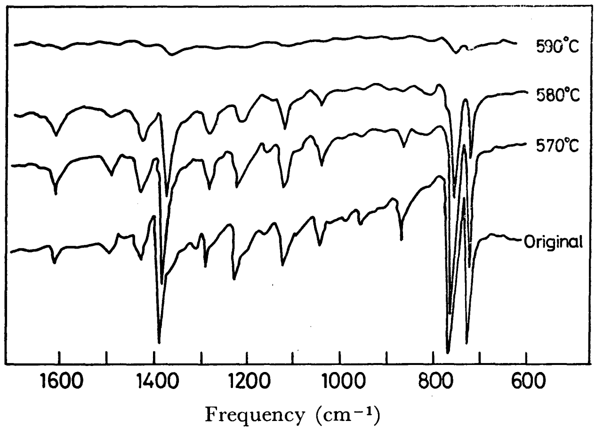

Fig. 3. Changes of IR spectra of PZ by heating under nitrogen.

Change of the infrared spectrum of PZ-1 by heating is shown in Fig. 3. We see that all bands, especially the two bands at 720 and 755 cm^{-1}, decreased remarkably at 580°C, a weak band appearing at 810 cm^{-1}.

Only the content of hydrogen decreased with temperature rise, from 34.8 to 32 atom% of sample treated at 580°C and 31.6 atom% treated at 600°C. Loss of a hydrogen up to 580°C and 600°C corresponds to 3—3.5 atoms of hydrogen per molecule. The content of nitrogen below 600°C remains almost the same as that of the original. Remarkable changes of X-ray diffraction profile were also observed at 580°C (Fig. 4). Below this temperature, the crystal structure of the original PZ is not greatly damaged, and 002 diffraction line appears at 580°C and grows with rising temperature.

The results of microscopic observation with crossed Nicols are shown in Fig. 5. The needle-like crystalline material

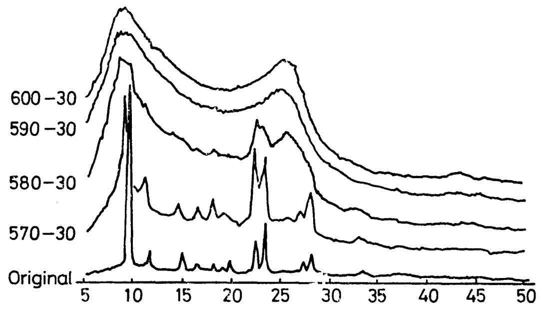

Fig. 4. Changes of X-ray diffraction profile with raising temperature. (Numbers show temperature (°C)—period (min)

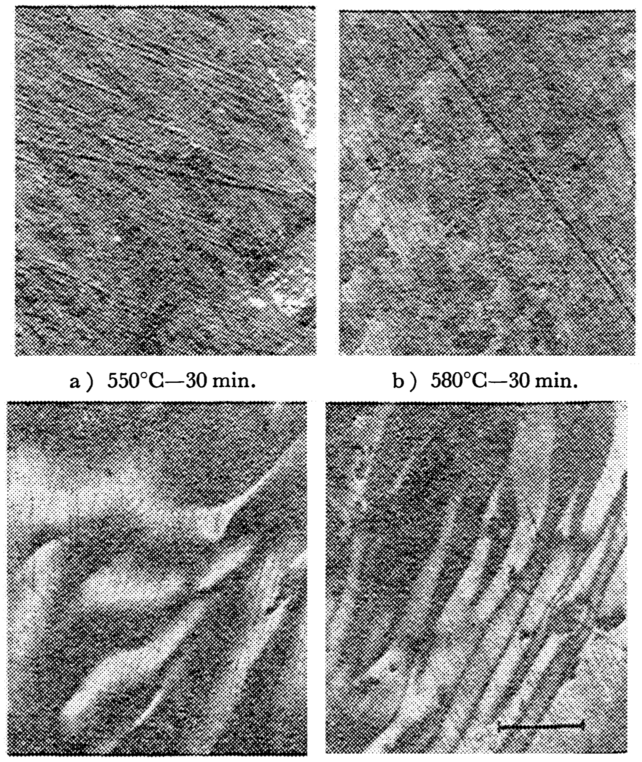
a) 550°C—30 min.
b) 580°C—30 min.
c) 590°C—30 min.
d) 600°C—30 min.

Fig. 5. Microscopic photograph with crossed nicols (Scale is 50 μ)

---

[16] J. Schmidt and J. Söll, *Ber.*, **40**, 2456 (1907).

(Fig. 5–a) appears to be converted into the oriented mesophase at 580°C (Fig. 5–c).

It has been found that pure PZ is converted into an anisotropic pitch-like material with a loss of about three hydrogen atoms per molecule. Since there are four overcrowed positions caused by four hydrogen atoms as shown in Fig. 6, the first step of dehydrogenation probably occurs at these positions and the plane dimer may be formed. Thus, it seems reasonable to consider that the pitch-like material formed at 580°C is mainly composed of a mixture of the monomer and the dimer, and the anisotropic structure caused by the interaction between these plane molecules.

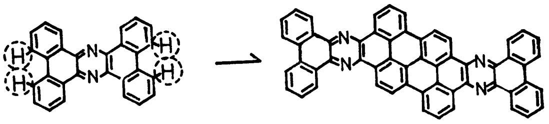

Fig. 6. Formation of dimer from PZ monomer.

PZ-2 crystal which contains some impurity gave the spinnable pitch-like material at lower heating temperature than that in the case of pure PZ-1 crystal. PZ-2 crystal was converted gradually into a black molten substance above 500°C. Spinnable pitch-like material was formed by heating under nitrogen at 530°C for 110 min. Various changes caused by heating in this case occurred during the process which was essentially the same as that for PZ-1.

Graphitizability of PZ Pitch. In order to determine the graphitizability of PZ pitch, the coke obtained was crushed and then heated under nitrogen at various temperatures below 2800°C. The coke made from PZ-1 pitch is a graphitizing carbon with interlayer distance d_{002} 3.361Å and crystallite thickness $Lc_{(002)}$ 850Å after 2800°C-treatment. PZ-2 pitch gave almost the same results as those of PZ-1 pitch.

Preparation of Carbon Fiber from PZ Pitch. The procedure was essentially the same as that previously reported.[12,17] In the case of PZ-2 pitch, the spinning temperature was 410—440°C and the spinning speed 300—400 m/min. It was better material than PZ-1 pitch from the viewpoint of spinnability and ability of conversion into an infusible fiber by oxidation. However, even in the case of PZ-2 pitch, its spinnability was not very satisfactory. The diameter of carbon fibers finally obtained was thus around 20 μ. This value is considerably greater than that of carbon fibers from petroleum asphalt, PVC pitch, and other pitch materials.[8,12,17] There was no difference between PZ-1 and PZ-2 pitch in the fundamental structure of the resulting carbon fibers. However, in mechanical properties, the carbon fiber from PZ-2 was better to some extent.

Carbonization was carried out under nitrogen up to the desired temperature below 2800°C. Heating rate was 5°C/min up to 1000°C and was 50°C/min above 1000°C. Throughout the process after spinning, heat treatment was carried out without mechanical stress.

Changes in Property with Heat Treatment. Changes in bulk density, electric resistivity and degree of preferred orientation of the basal planes are plotted in Fig. 7, and changes in crystal thickness(*Lc*), crystal size(*La*) and interlayer distance (d_{002}) in Fig. 8. It is noteworthy that the value of preferred orientation parameter is small. Even in the stage before heat treatment, it was only 23° and decreased to 6° with the rise in temperature. Since heat treatment was carried out with no stress, it is evident that the

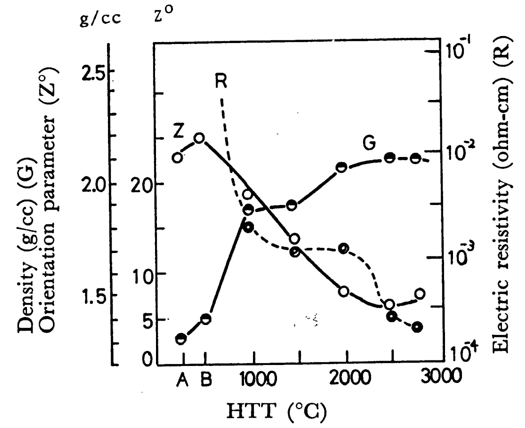

Fig. 7. Variations of the properties of PZ pitch fiber with raising temperature.
A: stage of pitch fiber
B: oxidized fiber

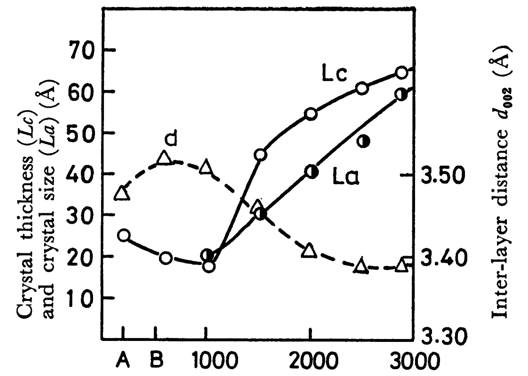

Fig. 8. Variations of the X-ray diffraction parameters of PZ pitch fiber with raising heat-treatment temperature.
A: stage of pitch fiber
B: oxidized fiber

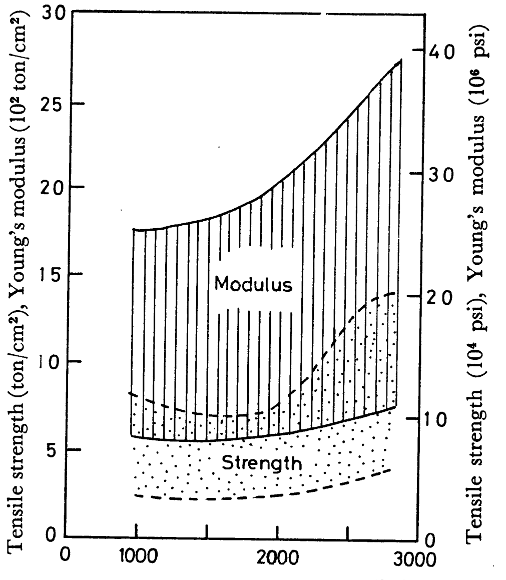

Fig. 9. Variations of mechanical properties of PZ pitch based carbon fiber with raising heat-treatment temperature.

---

[17] S. Otani, *Carbon*, **3**, 31 (1965).

TABLE 1. CHARACTERISTICS OF TYPICAL PITCH-BASED CARBON FIBERS

Characteristic	Pitch-based carbon fibers			PAN based carbon fiber
	Stretch-graphitized,		Non-stretch-graphitized PZ based fiber heated at 2800°C	RAE Type I
	G-1	G-2		
Orientation parameter (Z°)	9	8	6	8
Immersion density	1.85	1.75	2.08	2.01
Electrical resistance (ohm-cm)	5×10^{-4}	1×10^{-3}	4×10^{-4}	3×10^{-4}
Inter-layer distance (Å)	3.40	3.55	3.39	3.39
Crystal thickness (Å)	60	40	60	60
Young's modulus ($\times10^6$ psi)	70	45	20 (40)[a]	60
Tensile strength ($\times10^3$ psi)	300	420	120 (180)[a]	300

[a] Maximum value.

the progress of orientation is due to the nature of the original pitch material.

The mechanical properties, tensile strength and Young's modulus are shown in Fig. 9. The maximum Young's modulus reaches about 280×10^8 g/cm^2(40×10^6 psi), but the maximum tensile strength is only 13×10^6 g/cm^2(180×10^3 psi). We see that Young's modulus increases with the rise in heat treatment temperature, the tensile strength having a minimum at around 2000°C.

Discussion

X-Ray diffraction parameters and the properties of the three typical carbon fibers are given in Table 1. PZ-pitch based carbon fiber heated at 2800°C and PAN based high modulus one are identical in their characteristics except for mechanical properties. Stretch-graphitized carbon fibers G-1 and G-2 are characterized by their low densities. From the data of interlayer distance, crystal thickness and electric resistance, it seems that the crystal growth in G-2 is restricted to some extent as compared with other fibers.

The mechanical properties of the pitch based carbon fibers were remarkably improved by means of stretch-graphitization using higher temperature and greater stress. From the data in Fig. 2, it is seen that two kinds of carbon fibers, high modulus and high strength, were prepared from pitch based carbon fibers by this method. Since the two carbon fiber M and S were heat treated under almost the same conditions, it seems reasonable that their formation is attributed mainly to the nature of the original carbon fibers. However, no distinct difference between the two original fibers was observed in their mechanical properties and structure. This seems to result from the lack of an effective method to detect the difference.

PZ pitch is less spinnable, and PZ pitch fiber has less ability to be converted into infusible fiber by oxidation as compared with PVC pitch and petroleum pitch.[17,18] PZ pitch based carbon fibers we obtained were somewhat rough, their diameter being around $20\,\mu$. However, it has been found (Table 1) that the elemental nature, except for mechanical properties, of PZ pitch based carbon fiber is almost the same as that of PAN based high modulus fiber prepared by stretch-graphitization. Since PZ pitch based carbon fiber can be prepared without any stretching through the whole heating process, stretch-graphitization is not always necessary for preparing highly oriented carbon fiber, and thus the precursor nature has an essential effect on the structure of the fiber. Since Young's modulus of PZ pitch based fiber reaches 280×10^8 g/cm^2 (40×10^6 psi) in maximum value and 140×10^8 g/cm^2 (20×10^6 psi) in average value, one might say that PZ pitch based carbon fiber belongs to a high modulus, at least a middle modulus, carbon fiber. However, mechanical properties of the PZ pitch based carbon fibers are generally lower than those expected from their fundamental structure. It was shown that both Young's modulus and tensile strength were closely related to the diameter, increasing with decrease of the diameter.[17,18] When the diameter becomes smaller than $10\,\mu$, the mechanical properties are remarkably improved. Thus, the lower mechanical properties of PZ based fiber is expected to improve remarkably, if the PZ based fiber having smaller diameter than $10\,\mu$ is prepared. For this purpose, it should be noted that PZ-2 pitch containing some amount of impurities was more spinnable and was more easily converted into the infusible fiber than PZ-1 pitch.

Little attention has been paid to finding a new procedure which does not require stretch-graphitization. The authors think there is a fair prospect that high modulus carbon fibers can be prepared by use of a graphitization process without stretching from pitch composed of highly oriented constituent molecules.

The authors are indebted to Dr. E. Ōta for supply of the PZ crystal and for helpful discussions.

---

[18] S. Otani, K. Yamada, T. Koitabashi, and A. Yokoyama, *Carbon*, **4**, 425 (1966).