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The Preparation of Highly-oriented Carbon Fiber from Pitch Material

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In our previous papers[1–3] it was shown that carbon fiber can be prepared from pitch materials, moreover, Araki and Gomi[4] have succeeded in the production of carbon fiber from pitch material on a pilot-plant scale.

In the earlier reports[1,2] it was pointed out that the carbon fibers obtained from pitch had an isotropic structure and were "nongraphitizable." Recently, two methods for the preparation of highly-oriented carbon fiber from pitch material have been developed in our laboratory. One is a technique using a high-temperature treatment under stress in a range of temperature above 1800°C, while the second is a technique using a specific pitch-like material, such as pitch prepared from tetrabenzophenazine.

The object of this communication is to report some results obtained by the former method.

Experimental and Results

The original carbon fiber used in this work was prepared at 1000°C, on a pilot-plant scale, from a pitch which is a by product of the naphtha cracking process.[4] The high-temperature treatment was carried out under stresses ranging from 0.1 to 0.5 g per denier by the use of 2000—3000-denier bundles. The samples were heated by the use of a graphite-tube furnace in a stream of nitrogen and a rate of 125°C per minute up to 2500°C, which last temperature was maintained for about three minutes. A change in the length of the carbon fiber was clearly observed at temperatures over 1800°C, and it increased with increase in both the stress and the temperature applied. These results are shown in Fig. 1. The diameter of the carbon fiber finally obtained under a stress of 0.5 g per denier is 4.5—6.5 μ.

Stresses below 0.2 g per denier do not effectively improve the preferred orientation of crystallines. Improvement, however, gradually becomes clear with increase in the tension applied over 0.3 g per denier. In Fig 2, the intensity of the X-ray reflexion, $I(\phi)$, is plotted against ϕ, the angle between the C-axis of the reflecting crystallite and the fiber axis.

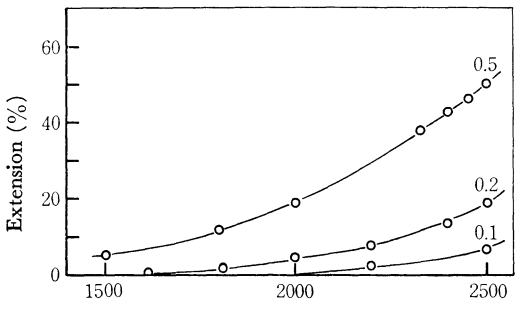

Fig. 1. Relation between the change in length and the stress applied at the heating process.
The numerals in the figure indicate the stress applied (g/denier).

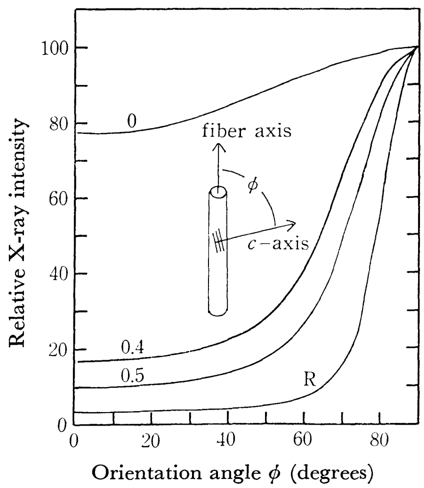

Fig. 2. Relation between the stress applied at the heating process up to 2500°C and the orientation of crystallites.
0: free from stress
0.4: stress of 0.4 g/denier
0.5: stress of 0.5 g/denier
R: RAE carbon fiber Type I (Control) Royal Aircraft Establishment

1) S. Ōtani, *Carbon*, **3**, 31 (1965).
2) S. Ōtani, *ibid.*, **3**, 213 (1965).
3) S. Ōtani and K. Yamada, *Kogyo Kagaku Zasshi*, **69**, 626 (1966).
4) T. Araki and S. Gomi, *Applied Polymer Symposia*, No. 9, 331 (1969).

The results shown in Fig 2 indicate that the majority of the layer planes in the fiber treated under a stress of 0.5 g per denier are oriented within 30° of the fiber axis. The interlayer spacing and the crystallite size of the filament are 3.45 Å and about 45 Å respectively.

Heat treatment under stress improves the tensile strength and the modulus of the carbon fiber. The average tensile strength and the average modulus of the original carbon fiber are 9.5×10^6 g/cm^2 and 650×10^6 g/cm^2 respectively. The average values of the carbon fiber prepared at 2500°C under a stress of 0.5 g per denier are 18.3×10^6 g/cm^2 in strength and 2100×10^6 g/cm^2 in the modulus.

Discussion

These findings on the mechanical properties are not satisfactory when compared with those from the best high-modulus or high-strength carbon fiber obtained from other materials. It was, however, confirmed that a high-temperature treatment under stress is effective in causing a preferred orientation of carbon crystallites, even when the carbon fiber is prepared from pitch materials. In general, the structure and properties of carbon fiber prepared from pitch materials vary with the type of raw pitch material used, the temperature and the period of preoxidation, the oxidizing atmosphere, *etc.* For example, when a pitch material prepared from tetrabenzophenazine, which possesses highly-oriented molecules,[5] is used as the raw material, the application of stress at the heating stage is not necessary to prepare a highly-oriented carbon fiber. On the contrary, when using pitch fiber spun at a low speed from PVC pitch, it is unlikely that a high orientation can be obtained even when the heat-treatment is carried out under stress.[6]

In these experiments, the application of the higher temperatures and the greater stresses was not possible because of the design of the furnace. However, from the results described above and from general information concerning high-modulus carbon fiber from PAN and rayon,[7] it is likely that further improvements can be expected by the use of a higher treatment temperature and a greater stress.

5) S. Ōtani and S. Watanabe, 9th Conference on Carbon at Boston, June, 1969, Summary of Papers (1969), p. 29.

6) S. Ōtani, A. Yokoyama and A. Nukui, *Applied Polymer Symposia*, No. 9, 325 (1969).

7) H. M. Ezekel, 9th Conference on Carbon at Boston, June, 1969.