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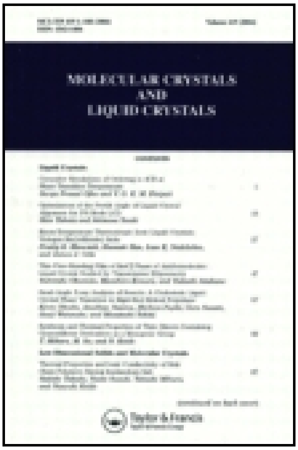

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Carbonaceous Mesophase and Carbon Fibers

S. Otani [a]

[a] Department of Chemistry, Faculty of Technology, Gunma University, Kiryu, Gunma, 376, Japan

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Carbonaceous Mesophase and Carbon Fibers†

S. ŌTANI

Department of Chemistry, Faculty of Technology, Gunma University, Kiryu, Gunma 376, Japan

(*Received October 22· 1980*)

1 INTRODUCTION

I esteem it a great honor to have been invited to this meeting. On the other hand, I am a little confused by the invitation, because I am *not* a specialist in liquid crystals but only in carbon materials. The main reason why I have been invited to this meeting is, I think, probably because I first originated the fundamental procedure for producing carbon fibers from pitches and have been developing this field for the past 15 years.[1–12] I also presume that the preparation of carbon fibers from mesophase pitches especially claims your interest. From these points of view I have prepared the subject matter of my lecture.

In this lecture, I would like firstly to describe the history of pitch-based carbon fibers from their origin to the present time. Secondly, I will describe how the early carbon fibers obtained from pitches evolved into high performance grade materials. Finally, I will make a few remarks concerning those areas in which we still lack understanding.

2 THE BEGINNING OF CARBON FIBERS FROM PITCHES

In August 1963, we were investigating the preparation of activated carbon from lignin. When lignin powder was heated in a flask up to 500°C in a stream of air by using an apparatus such as that shown in Figure 1, a number

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† Invited lecture, presented at Eighth International Liquid Crystal Conference, Kyoto (Japan), June 30–July 4, 1980.

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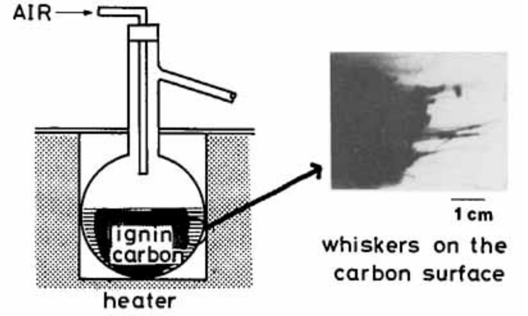


FIGURE 1 Whiskers which marked the beginning of lignin and pitch based carbon fibers

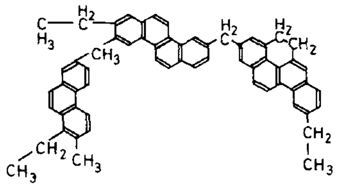
of whiskers were found on the surface of the carbonaceous product obtained. The photograph on the right-hand side of the figure is that of the whiskers obtained. I was very interested in this phenomenon and hypothesized on the formation of the whiskers.

I thought at that time that some spinning molten product first would form in a region near to the flask wall in the early stage of the heating, and would be stretched between the flask wall and the pyrolysed lignin as sintering progressed; then the whiskers formed by stretching would be oxidized into infusible whiskers at the subsequent heating stage. In order to confirm this hypothesis, some samples of lignin powder were rapidly heated till they melted in a porcelain crucible; then I dipped a fine stick into the molten lignin, and pulled it out quickly. As expected, the molten product had a good spinnability and a fine filament was formed at the end of the stick. The lignin filaments (about 20 cm in length) thus obtained were easily converted into an infusible state by heating in air up to 300°C. The first lignin-based carbon fiber was successfully prepared from these infusible filaments by further heating up to 1000°C under nitrogen.

In those days, we had also been investigating the carbonization mechanism of pitch materials. The pitch used in the series of investigations was most often a polyvinyl chloride (PVC) pitch formed from PVC powder by heating under nitrogen at 400°C.

PVC pitch is a very complex mixture of polynuclear aromatic molecules and the molecular structure,[2] including most of the characteristic configurations, is thought to be as shown in Figure 2. PVC pitch has the highest softening point compared to other pitches, and its H/C atomic ratio and mean molecular weight are in an intermediate range.

At that time, I felt that carbon fibers should be able to be prepared from PVC pitch as well as from lignin. The same examination as that applied to lignin was attempted using the PVC pitch. As expected, molten PVC pitch was found to be more suitable for carbon fiber preparation than lignin. Both



H/C	0.5~0.6	0.8	1.3~1.6
MW	260~280	800	800~1000
SP	60~70	180	75~90
(°C)	coal tar pitch	PVC pitch	petroleum asphalt

FIGURE 2 Molecular structure of PVC pitch and a comparison with other pitch materials

preliminary examinations of the lignin and the pitch were carried out in one day. Therefore, I think both the carbon fibers, lignin-based carbon fiber[1,13] and pitch-based carbon fiber, are, so to speak, twin brothers.

The opportunities presented by the production of carbon fiber from lignin were realized at an earlier date than those of pitch-based carbon fiber. However, the production of lignin-based carbon fiber was discontinued from 1973; whereas, on the other hand, production of pitch-based carbon fiber has developed in the order shown in the Table I, and is now on the market.

It was very lucky for me that the first examination was attempted using PVC pitch because, according to many investigations carried out after that, PVC pitch is the only material which does not need any pretreatment prior to spinning. In order to be able to use all other bituminous materials, some

TABLE I

Chronological table of lignin and pitch based carbon fibers

Lignin based carbon fiber	
1963	Beginning
1967	Market the product (Nihon Kayaku Co.)
1973	Discontinued
Pitch based carbon fiber	
1963	Beginning[1]
1965	Fundamental procedure by use of PVC pitch
1967	Utilisation of other pitches[4, 5, 7]
1970	Market the product[5]
1980	300 ton/year

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special treatments are required prior to their spinning. Therefore, if I had used other pitch materials than PVC pitch in the first attempt, I would not have succeeded in my attempt to make carbon fiber from pitches.

3 THE FUNDAMENTAL PROCEDURE

Figure 3 shows the fundamental procedure[2] of carbon fiber production from pitches. The available pitch for carbon fiber preparation by this procedure generally requires a higher melting point than 180°C and a good spinnability. If the melting point of the pitch is below this temperature, it becomes very difficult to prepare the infusible fiber without any trouble in the subsequent oxidation process. For this reason, ordinary tar or pitches need to be treated by heating and/or extraction prior to spinning.[3,4,6]

Figure 4 shows the apparatus[2] and conditions for melt spinning. All experiments in our laboratory have been carried out by use of such simple apparatus. Molten pitch filament extruded from the pin hole is stretched into a fine filament during the winding.

All pitch materials used in the early experiments described above were not carbonaceous mesophases, but optically isotropic pitches.

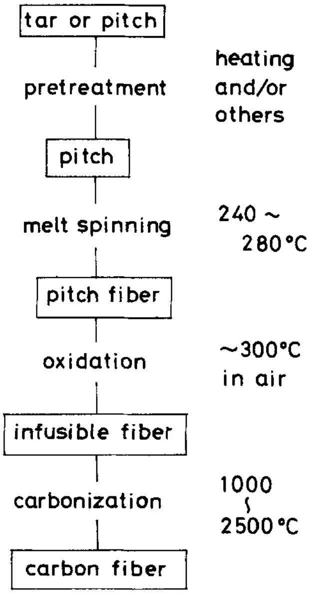

FIGURE 3 Fundamental procedure for pitch based carbon fiber.

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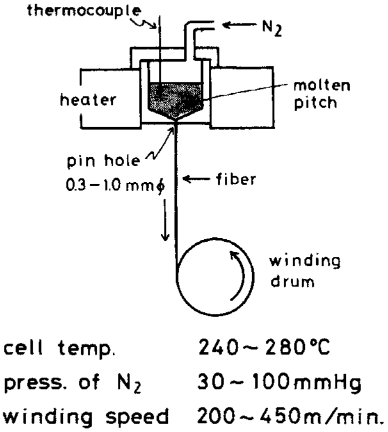

FIGURE 4 Apparatus and conditions for melt spinning.

The continuous mass production[14] of pitch fiber has been carried out by using a spinning machine of the centrifugal type instead of the extruding type shown in Figure 4.

4 LOW MODULUS TYPE AND HIGH PERFORMANCE TYPE

It is well known that carbon fibers are classified as low modulus type or high performance type according to their mechanical properties as shown in Table II. According to this classification, all carbon fibers described above belong to the low modulus grade.

Until recently, low modulus fibers have been used as thermal insulation at a high temperature, gaskets, and filters in various plastics. Now it is believed that these fibers offer very promising prospects for the electrode material of hydrogen-oxygen fuel cells and as substitute materials for asbestos in various Portland cement products and the brakes of automobiles. Future demand for the low modulus fibers seems to be determined by the consumption as a substitute for asbestos.

The second group, the high performance fibers, are used as reinforcing elements in plastics, especially epoxyresins, and are certainly extending their markets in the area of aerospace application. Future demand for the fibers will be influenced greatly by their applications in automobiles as well as in aerospace. At the present time, the great majority of high performance fibers is produced from polyacrylonitrile (PAN) fiber. Much attention, however, is focused upon whether it will be possible to produce low price and high performance carbon fibers commercially from pitches, because low price fibers

TABLE 2

Comparison of the two carbon fibers

Type	Low modulus (LMCF)	High performance (HPCF)
Strength (Kg/mm^2)	90–85	300–300
Modulus (10^3 Kg/mm^2)	4.2–3.8	50–20
Present use	Insulation, gasket, fillers in plastics	Reinforcing elements (sporting goods, aerospace)
Future use expected	Substitution for asbestos, electrodes	(Automobile and others)

are indispensable in order to open up such large new fields of application as that in automobiles.

The difference in the mechanical properties of the two types of fiber, of course, corresponds to that of their structures. The pictures in Figure 5 are polarized light micrographs of both types of carbon fiber. The low modulus fiber exhibits a distinct preferred orientation along the fiber axis. The essential factor in the technique for preparing the high performance carbon fiber is in how the desired, preferred orientation is achieved. There are two different ways of doing this. One of them is by stretching which is carried out during each or all of the heating processes during oxidation, carbonization, and/or

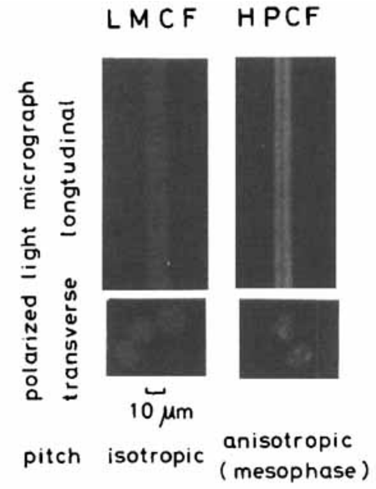

FIGURE 5 Polarised light micrographs of a cross-section of carbon fibers.

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graphitization. This technique[8,9] is recognized to be most effective for the preparations from PAN fiber, but does not offer much advantage for the pitch fiber which is very brittle in the early stage of carbonization. The other technique is the so-called "mesophase process" which has been developed for pitch fiber.[10] The most essential point of this technique is the utilization of an anisotropic pitch, the so-called carbonaceous mesophase, instead of the isotropic pitch which is used for low modulus carbon fiber.

5 MESOPHASE PITCH

When non-volatile organic compounds are heated under an inert atmosphere, the general pattern of behaviour has been found to be as shown in Figure 6. The substance melts on heating and becomes an isotropic pitch or liquid. As the temperature rises over about 350°C, optically anisotropic spheres appear in the isotropic matrix. This optically anisotropic phase is called a carbonaceous mesophase. With the increase of temperature, and to a certain extent with time delay at a fixed temperature, the anisotropic spheres grow larger and coalesce. Coalescence of spheres develops to give the continuous phase, followed by solidification to form semicokes. The optimum pitch materials for the preparation of the low modulus carbon fibers discussed above belong in the final stage of the isotropic pitch.

Figure 7 shows polarized light micrographs of mesophase growth from the initial to the final stage. These pitches are two-phase emulsion systems in the molten state at high temperature. The continuous phase is isotropic in the initial stage and anisotropic in the latter stage.

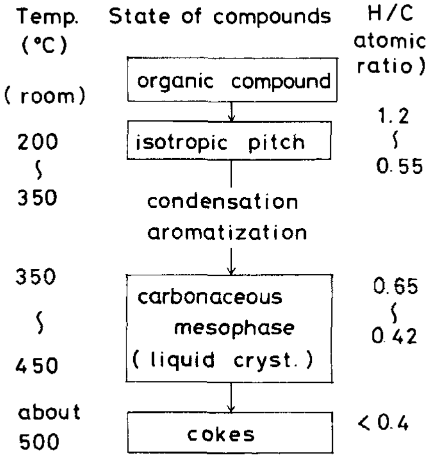

FIGURE 6 Change in non-volatile organic compounds brought about by heating.

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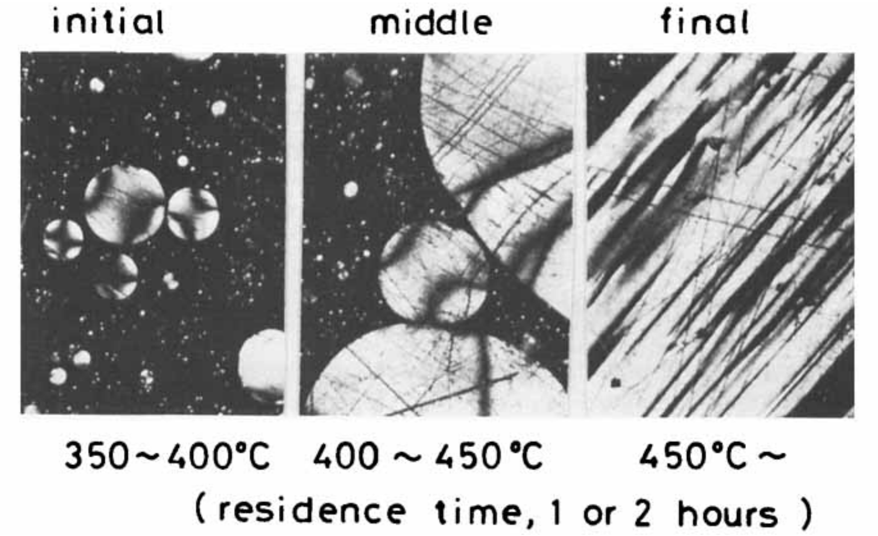

FIGURE 7 Standard path of mesophase growth

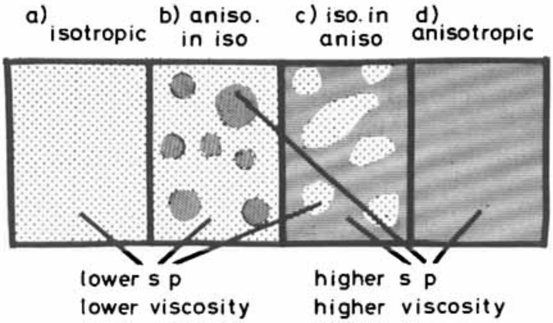

FIGURE 8 Phase inversion of a pitch.

Figure 8 represents schematically the phase inversion of the pitch with rising temperature. The isotropic pitch (a) can be spun easily to give a filament, while the pitches of the two-phase emulsion types (b) and (c) are difficult to spin. The primary cause of the difficulty, I think, is the remarkable difference between the softening point and viscosity of the anisotropic and isotropic phases. The melting point and viscosity of the anisotropic phase, of course, are generally higher than those of the isotropic phase. From this reason, the anisotropic spheres of the (b) type emulsion often behave like solid particles at the temperature at which the continuous isotropic phase shows the optimum viscosity to be spun. However, in the case of the (c) type emulsion, such

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behaviour is not observed; the viscosity of the pitch is generally too high to spin by use of the simple spinning apparatus described above.

6 CARBON FIBER FROM MESOPHASE PITCH

In 1968, Professor Ota, who is an organic chemist and co-worker in our group, proposed an investigation of the carbonization of tetrabenzophenazine shown in Figure 9. Up to that point, we had been interested in the carbonization mechanisms for large condensed aromatic systems in addition to carbon fiber preparation. Tetrabenzophenazine was prepared for another investigation carried out before that time. I will call it PZ for short. This compound is very interesting. The compound appears to be converted directly into the bulk mesophase, without spheres being formed, at temperatures over 500°C which change with the purity of PZ. Using highly purified PZ, the conversion occurs over 580°C. In this case, no isotropic pitch-like material is observed; that is, a two-phase emulsion does not appear. The melting point of the resulting pitch is about 370°C. J. D. Brooks and G. H. Taylor[16] also reported previously that dibenzanthrone (shown in Figure 1) is converted into the mesophase in the same way. The pitch from dibenzanthrone, however, is too viscous to be spun. On the other hand, the molten mesophase pitch from PZ has good spinnability, in spite of its relatively high melting point, and it can be spun at a temperature around 400°C by use of the simple spinning apparatus described above. The reasons why this mesophase pitch exhibits a relatively low viscosity and a good spinnability are still obscure.

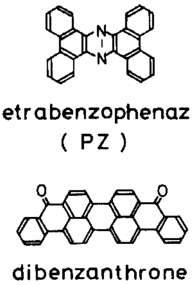

FIGURE 9 Molecules of tetrabenzophenazine and dibenzanthrone

We did not investigate this mesophase further from the view point of liquid crystals, but in 1968, tried to make a high performance carbon fiber from this pitch.[10] Figure 10 is a polarized light micrograph of the pitch used at that time. The coarse, flow-type texture appears all over the surface of the pitch.

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Polarized light micrograph of PZ pitch

spinning conditions

	PZ pitch	isotropic pitch
cell temp.(°C)	410	240~280
press. of N_2 (mmHg)	100	30~100
winding speed (m/min)	350	200~450

FIGURE 10 Pitch from tetrabenzophenazine and its spinning conditions.

The spinning conditions are shown at the bottom of Figure 10, together with the conditions applied to the isotropic pitch. All treatments after spinning are essentially the same as those applied to the isotropic pitch fiber described above.

The fibers in their as-spun state are highly oriented, with the molecular layer planes aligned along the fiber axis. Figure 11 shows the arcs of the 002 reflection for a plate X-ray diffraction pattern taken with the beam perpendicular to the fiber axis. The preferred orientation of the layer planes was improved further with elevation of the heat-treatment temperature.

Changes in other properties, electrical resistivity, and density, are plotted against the heat-treatment temperature in Figure 12. These changes are almost similar to those for graphitizing carbon. The first highly oriented carbon fiber obtained in this experiment was thought to be somewhat deficient in its mechanical properties, especially tensile strength, as compared with those from polyacrilonitrile. But on the basis of these results, I had adequately confirmed the possibility of producing high performance carbon fiber from mesophase pitches. The first preliminary report on this subject was presented at the annual meeting of the Chemical Society of Japan held in 1969.

The mesophase pitch from PZ was highly graded as an excellent material for a high performance fiber and we directed out efforts to using other convenient mesophase pitches for this purpose. After a few months, the group working at the Kureha Chemical Industry Co. which had carried out joint

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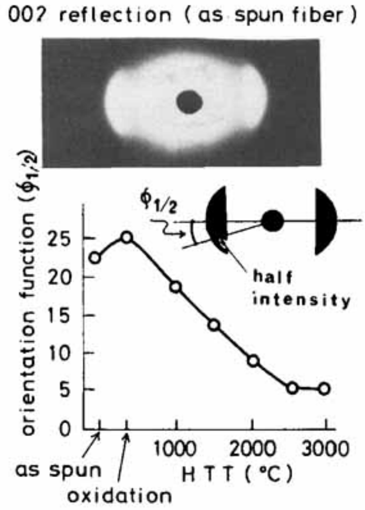
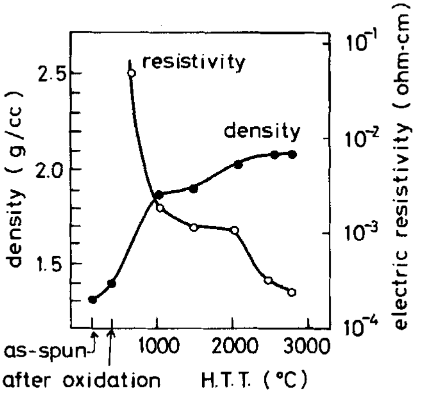


FIGURE 11 Preferred orientation of PZ pitch fiber.

research with us informed me that they had achieved success in the utilization of a petroleum cracking residue to make a high performance carbon fiber.[11] The mesophase pitch prepared by the heat-treatment at 410°C for 5 hours is not a monophase liquid such as the PZ pitch, but a two-phase emulsion in which the continuous phase is anisotropic.



mechanical properties (2800°C)	
modulus	25×10^3 kg/mm^2
strength	130 kg/mm^2

FIGURE 12 Properties of carbon fiber from PZ pitch.

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The viscosity against temperature curve of the mesophase pitch is shifted to about 100°C higher in temperature than that of the isotropic pitch used for low modulus carbon fiber, as is shown in Figure 13. The viscosity, however, was thought to be considerably lower than that of other mesophase pitches. This fact probably indicates the excellent compatibility of the two components of the emulsion. The spinning temperature was about 370°C. The spinning apparatus used for this mesophase pitch was essentially similar to that used for the preparation of low modulus fibers.

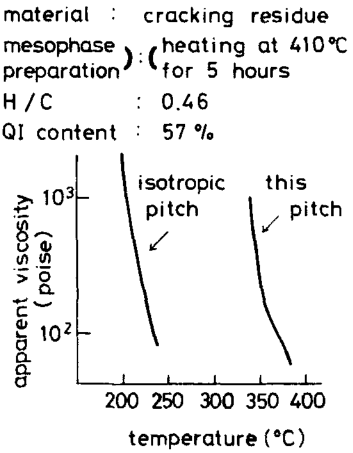

FIGURE 13 Viscosity against temperature curve for the mesophase pitch from a cracking residue.

The pitch fiber obtained, of course, exhibits a highly preferred orientation of the layer planes. The changes in the degree of orientation, density, and electrical resistivity with increase of heat-treatment temperature are similar to those observed in the case of the PZ pitch. The mechanical properties[13] are plotted against heat-treatment temperature in Figure 14. The modulus is remarkably increased over 2000°C. The tensile strength is at its maximum at 1500°C and then exhibits a tendency to decrease, the extent of which seems to be closely related to the texture seen with the optical microscope on observing the transverse section of the carbon fiber.

7 STRUCTURE OF THE HIGH PERFORMANCE FIBER FROM THE MESOPHASE PITCH

A recent detailed study on the structure of this carbon fiber was reported by M. Inagaki and his co-workers.[17] According to their results, this fiber heat-

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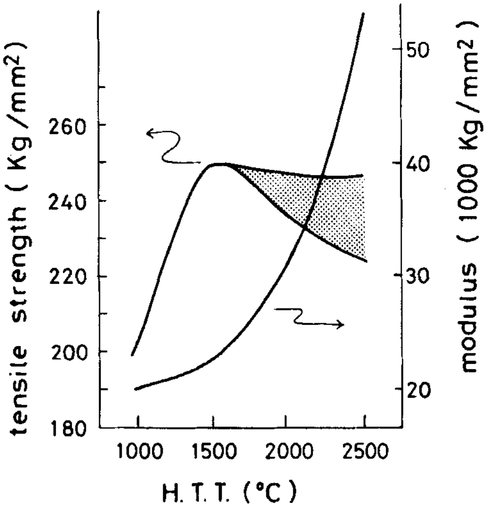

FIGURE 14 Mechanical properties of high performance carbon fiber from pitch.

treated over 2500°C has a higher degree of graphitization and preferred orientation than that of a high performance carbon fiber obtained from a PAN fiber with the high temperature stretching technique. Next, its graphitizability seems to be related to the texture of the transverse section. Finally in the fiber heat-treated at low temperature, porous regions with small and randomly oriented layers coexist with regions with well developed layers; the former being hard and carbon-like and the latter soft and carbon-like in their microstructure and their change with heat-treatment. The two regions of carbon fiber may be responsible for the two phases of the mesophase pitch. These results suggest that the characteristics of a mesophase pitch and the spinning conditions affect the fundamental structure and properties of the carbon fiber made from it.

8 PROBLEMS REMAINING TO BE SOLVED

Members of the Kureha Chemical Industry Co. have told me that techniques for the mass production of high performance carbon fiber from the mesophase pitch nearly approach perfection. At present, however, the pitch-based high performance carbon fiber is still not supplied commercially in Japan, and only very limited amounts are supplied tentatively.

Union Carbide has also been developing various types of high performance fiber from mesophase pitches and has recently begun to supply products. I have no detailed information of these fibers named "Thornel P" or "Thornel matt". As far as I know, basic knowledge about and techniques for the mass production of high performance carbon fibers from mesophase pitches have not reached their final goals either in Japan or the United States at the present point in time.

It seems to me that there are many areas in which we are still deficient in understanding. Improvement of the tensile strength is the first, and this is a pressing problem awaiting solution. The basis of a solution is an understanding of the relations between the properties of the carbon fibers and their structures. The fine structure of a pitch-based fiber which can be observed with the high resolution electron microscope is more complicated than that of a PAN-based fiber. A typical example of the complexity is the co-existence of the two different fine-structure regions previously described. The complications are also made greater by the texture which can be observed with the optical microscope. Both Inagaki[17] and Singer[18] have suggested independently that the texture of the transverse section of the fibers affects their graphitizability and other properties. In order to control the texture, the relations of the nature of the mesophase, the spinning conditions and the fiber structure must be clarified.

The next problem, the nature of the carbonaceous mesophase (i.e., the liquid crystalline state) is, of course, most fundamental. There have been many phenomenological investigations of such mesophases up to the present time, but it seems to me that this knowledge is still not systematized. Moreover, how do we systematize the knowledge of mesophases which are very complex mixtures of polynuclear atomatic molecules? This problem is only beginning to be explored.

The minimum mesophase requirements for carbon fiber preparation are good spinnability and good thermal stability during the residence time at the spinning temperature. These minimum requirements may be fulfilled on the basis of phenomenological investigations, but in order to realise excellent properties and high productivity, many problems still remain to be solved.

It is certain that the elucidation of these problems will make important contributions to the production of high performance carbon fibers from mesophase pitches. I hope that in the near future the techniques of mass production of this fiber will reach perfection through the support of research in the field of liquid crystals.

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