Carbon Fibers and Their Composites

Kensuke OKUDA*

Abstract

A brief history of carbon fibers and their application is reviewed.

The existing situations of the types of carbon fibers on the market and the performance of typical products are summarized, and the technical issues on production introduced.

Major applications are outlined.

* Kureha Chemical Industry Co., Ltd., 1-9-11 Nihonbashi-Horidome-cho, Chuo-ku, Tokyo (103), Japan

1. Introduction

Application fields of carbon fibers have expanded remarkably in the past fifteen years, through progress in the production technology and composite materials.

There have been very significant improvements in the performance of carbon fibers on the market, together with the development of new types of carbon fibers. For example, high strain-to-failure fibers with high strength and ultra-high Young's modulus fibers have come into the market. Moreover, activated carbon fibers, which are characterized by excellent absorption power, have been manufactured on a commercial scale.

Carbon fiber reinforced plastics (CFRP) have been widely used for sporting goods, aircraft structures, machine parts and so on. The construction industry has been applying light-weight concrete fortified with chopped fibers to large-sized buildings for several years.

In this paper, we report a brief history and the existing situation of carbon fibers and their composites laying stress on recent advances in the performance of the fibers.

2. A Brief History of Production and Application of Carbon Fibers

Carbon fibers which are used as reinforcements or fillers are usually classified into two types. One is the general-purpose type carbon fibers whose structure is isotropic. The other is the high performance type carbon fibers which are characterized by a high modulus of elasticity. Besides these, a third type of carbon fibers, activated carbon fibers shall be added to the family. They are distinctly different from the above ones in nature and application and were commercialized around ten years after high performance fibers.

In 1959 Union Carbide Corp. (Amoco Performance Products, Inc., presently) began commercial production of "graphite" cloth as well as other fibrous forms by baking rayon cloth and so on in an inert atmosphere to approximately 900°C, followed by graphitizing to temperatures usually higher than 2,500°C [1) 2)] (Fig. 1). These fibers belong to the general-purpose type and were quickly applied to ablation materials for space development.

Union Carbide also introduced the first high performance carbon fiber from rayon precursor to the market in late 1965 [3)]. These rayon-based high modulus "graphite" fibers, however, disappeared a few years later because of high processing cost in relation to their performance.

Just before this, Shindo developed a new process for preparing a carbon fiber from polyacrylonitrile (PAN) [4)], and this invention led to the commercial production of PAN-based general-purpose fibers by Nippon Carbon Co. in 1962.

After Shindo, Jonson et al.[5)] succeeded in obtaining high performance fibers from PAN by a method of improving the superstructure. These fibers, which were immediately applied to the turbine blades of the Rolls-Royce RB.211 turbofan engines and now account for a large percentage of the present demand for carbon fibers, came into the market in 1967 in U.K. and in succession Toray Industries entered into production with advanced technology[6] in 1971.

Early in 1970, based on the pioneering studies by Otani[7], the first manufacturing plant for general-purpose carbon fibers derived form petroleum pitch sources began operation on a scale of 120 tpa at Kureha Chem. Ind.[8]. Meanwhile, Otani also published a paper on a high performance fiber derived from anisotropic pitch[9]. High performance fibers from pitch, however, were commercialized by U.C.C. in 1976[10].

Applications of CFRP to sporting goods such as golf clubs and secondary structures in military aircraft in the early 1970s caused PAN-based high performance fibers to take off as industrial products. Accordingly many enterprises have successively entered into the market.

Advanced composite materials (ACM), in particular carbon fiber based ACM, have also been used for secondary structures in large-sized passenger aircraft and even for primary structures in military aircraft and small-sized civil airplanes such as the Voyager in the 1980s, and moreover some of them have been qualified as materials for primary structures in next generation aircraft, which shows that the aerospace industry could be a huge market for high performance carbon fibers.

Just after the second oil crisis, many firms and institutes began to study pitch-based carbon fibers, in particular high performance fibers. Some of the firms have constructed commercial plants on a scale of the order of 100 tpa.

Applications of pitch-based carbon fibers are quite different from those of PAN-based high performance carbon fibers. Until quite recently, application of general-purpose types from pitch was limited to thermal insulating materials, sealing materials, reinforcements for engineering plastics and the like. In 1983, they were used for construction materials, which are expected to provide a growing market for them. Also, pitch-based high performance fibers whose major application is at present space equipment will be used in the same application fields as those of PAN-based high performance fibers.

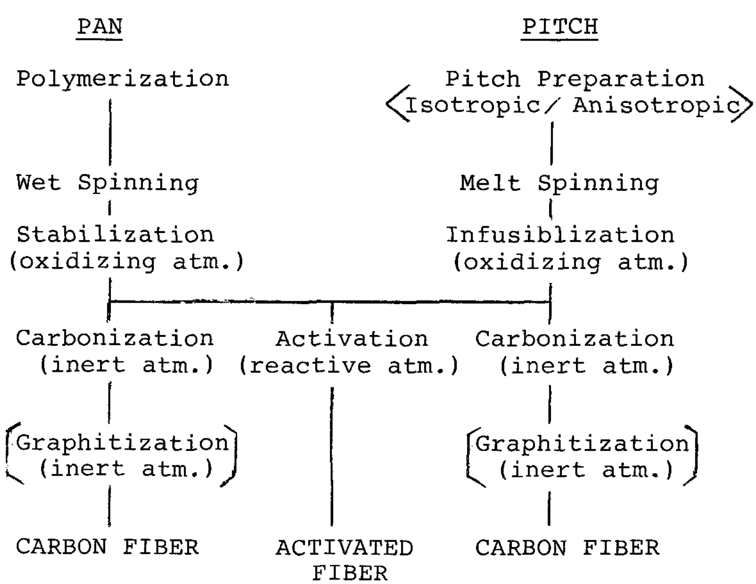
In the mid-1970s, an activated carbon of fibrous form which was named activated carbon fiber was developed in Japan[11], in order to utilize more effectively the adsorption function of carbon. Activated carbon fibers have been pursued by several firms ever since and have been attracting public attention from the ecological point of view.

Over the last ten years, some enterprises have been developing new types of carbon fibers, which are prepared directly from low molecular weight hydrocarbon compounds in the vapor phase and are named for vapor-phase-grown carbon fiber.

3. Progress in Production Technology and Mechanical Property of Carbon Fibers

Most of the carbon fiber products on the market are from PAN and pitch source, and rayon-based fibers are one small portion. The performance of the products has been improved significantly in response to materials requirements which advance with the expansion of application.

Before entering into this subject, I summarize the basic process for manufacturing carbon fibers from PAN and pitch below:



Prior to carbonization, precursor fibers, which are fabricated through conventional spinning technique, are stabilized (for PAN)/infusiblized (for pitch) in an oxidizing atmosphere. Stabilized PAN fibers/infusiblized pitch fibers are converted to carbon fibers by baking them in an inert atmosphere, and then graphitized if necessary.

The most important characteristic feature of both PAN and pitch is that the originally formed fiber structure of presursor fibers is kept through whole process, in other words, we can obtain the carbon fibers having preferred orientation which is one of the necessary conditions for giving excellent mechanical property.

In the case of pitch, isotropic pitch gives an isotropic fiber which belongs to the category of general-purpose carbon fibers, while if anisotropic pitch is used as precursor high performance fiber having the fiber structure is obtained.

Activated carbon fibers are manufactured by activating stabilized PAN fibers and infusiblized pitch fibers with for example steam at elevated temperatures, where activation means formation of a great number of open micropores which act as adsorption sites.

The tensile strength of the PAN-based high-strength type carbon fiber first marketed in 1967 was only 2,500 MPa with around 200 GPa of Young's modulus, as seen in Fig. 1, where the plotted value of Young's modulus of 400 GPa is for a high modulus type fiber. The mechanical pro-

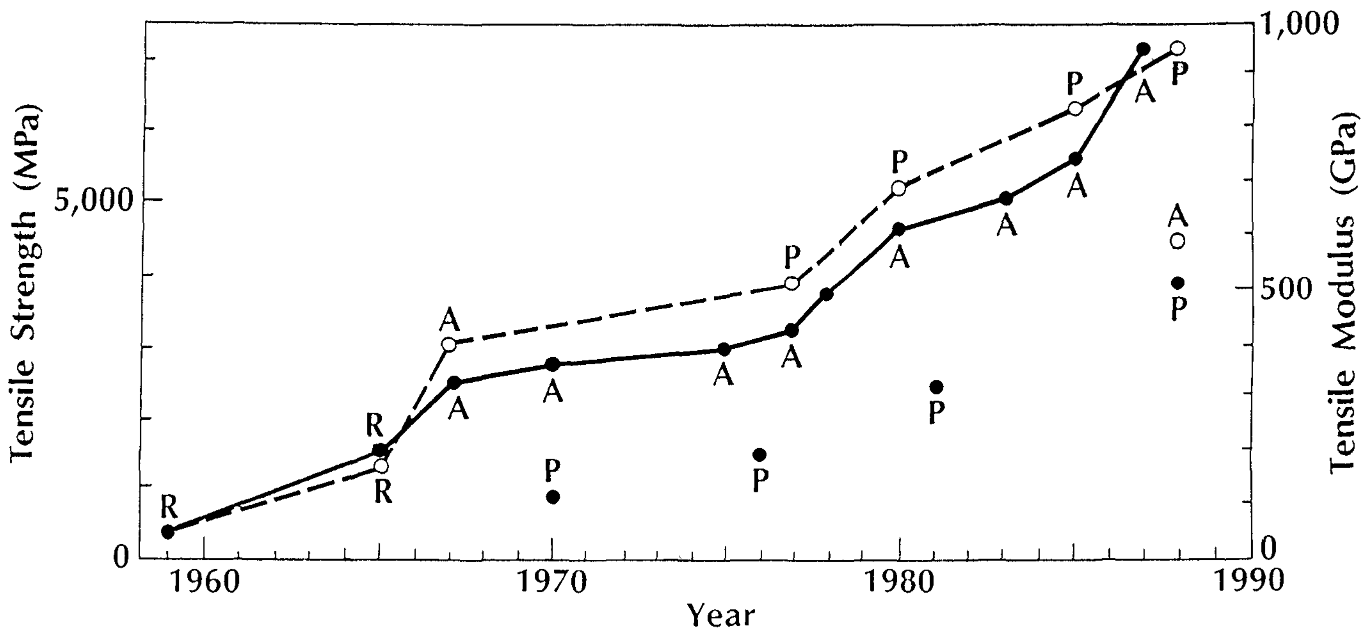


Fig. 1 Improvement in mechanical property of carbon fibers (maximum values of the fibers on the market)
solid line: tensile strength dotted line: tensile modulus of elasticity
A: PAN, P: pitch, R: rayon

perty of PAN-based fibers improved little till the middle of 1970s, because their applications were limited to sporting goods, artificial satellites and so on. From that time on, profound changes have steadily taken place in the production technology of carbon fibers, including pitch-based carbon fibers (see Fig. 1).

Since the application of ACM to primary structures in civil aircraft was projected at the beginning of 1980s, related industries have been extensively developing advanced CFRP whose material requirements are, for example, design strain equal to that of aluminum alloy for aircraft structures, high damage tolerance, higher specific modulus of elasticity and so on. These material requirements of CFRP can be, in terms of the reinforcing fibers, increase in strain-to-failure with high modulus of elasticity, improvement in the interface property, increase in heat resistance and so on, which improvement has been brought about through the development efforts of the fiber manufacturers. For instance, as illustrated in Fig. 1 and Table I, a fiber T-1000 having strain-to-failure over 2% with modulus of elasticity of 300 GPa came into the market in 1987. The tensile strength of this fiber is twenty times higher than that of the first fiber from rayon and twice as high as that of the standard grade of PAN-based high strength type fibers, e.g., T-300. Quite recently, new types of fibers have been developed in the PAN-based family; an intermediate modulus type fiber MRE 50 which is high in Young's modulus and also thick in diameter compared with the same type fibers, and

Table I Physical Properties of Carbon Fibers on the Market

Type	Fiber Designation	Tensile Strength (MPa)	Tensile Modulus of Elasticity (GPa)	Elongation at Break (%)	Diameter (μm)	Manufacturer
GP	T-101S	720	32	2.2	14.5	Kureha Chem.
	T-201S	690	30	2.1	14.5	"
	S-210	784	39	2.0	13	Donac
		(686)	41	1.6		Ashaland
	GF-20	980	98	1.0	7 ~ 11	Nippon Carbon
HP (PAN)	T-300	3530	230	1.5	7.0	Toray
	T-400H	4410	250	1.8	7.0	"
	T-800H	5590	294	1.9	5.2	"
	T-1000	7060	294	2.4	5.3	"
	MR 50	5490	294	1.9	5	Mitsubishi Rayon
	MRE 50	5490	323	1.7	6	"
	HMS-40	3430	392	0.87	6.2	Toho Rayon
	HMS-40X	4700	392	1.20	4.7	"
	HMS-60X	3820	588	0.65	4.0	"
HP (pitch)	P-25	1400	160	0.9	11	Amoco
	P-75S	2100	520	0.4	10	"
	P-120S	2200	827	0.27	10	"
	E-35	2800	241	1.03	9.6	du Pont
	E-75	3100	516	0.56	9.4	"
	E-130	3900	894	0.55	9.2	"
	F-140	1800	140	1.3	10	Donac
	F-600	3000	600	0.52	9	"
ACF	FX-100	2 g/d	500 a)	18 b)	15	Toho Rayon
	FX-600	<1 g/d	1500 a)	50 b)	7	"
	A-10	245	1000 a)	20 c)	14	Donac
	A-20	98	2000 a)	45 c)	11	"

a) specific surface area (m^2/g)
b) adsorption amount of benzene (%)
c) adsorption amount of acetone (%)

an ultra-high modulus type fiber HMS-60X with fairly high strength (see Table I). These results were achieved by improving the total process from precursor to finishing, such as increase in molecular weight and thorough purification, optimization of superstructure of PAN fibers, surface modification of carbon fibers, optimum process control and the like.

Besides reinforcements, high performance matrix resin which is tougher and more stable to temperature and humidity than conventional ones has been developed, because we cannot reach the material requirements mentioned above by means of improvement in the fiber performance only, as will be touched upon later.

Concerning pitch-based carbon fibers, significant advancement in the production technology has realized improvement in the mechanical property of high performance type fibers, as seen in Fig. 1 and Table I. For example, du Pont has introduced an ultra-high modulus type fiber E-130 whose Young's modulus is almost 900 GPa with 3,900 MPa of tensile strength. This Young's modulus value is over 80% of the theoretical value of graphite single crystal and twenty times higher than that of the rayon-based fibers commercialized first, and the tensile strength is improved two times or more higher than those of early pitch-based high performance type carbon fibers, for example, P-25, P-75S and others.

Four different types of basic superstructures or some modifications of them exist in pitch-based carbon fibers because of anisotropic nature of the constituents of carbon. In principle, the mechanical property of pitch-based carbon fibers depends on the superstructure which is formed in the spinning process and maintained through the whole subsequent process, in other words, one of the necessary conditions for obtaining fibers that have higher tensile strength is to control the superstructure.

Since the superstructure can vary substantially according to the nature of precursor pitch and processing, in particular spinning conditions, the development work on pitch-based carbon fiber is concentrated on improvement or modification of precursor pitch, whose typical preparation methods are summarized in Fig. 2. The early products such as P-75S are from conventional mesophase pitch[10]. New types of pitches other than conventional mesophase pitch give higher tensile strength than the latter, though each of the former is different in nature depending on preparation method; neomesophase[12] belongs to the same category as conventional mesophase pitch, and domant anisotropic pitch[13] and premesophase pitch[14] have a rather naphthenic nature, which is caused by hydrogenation applied in any stage of the processes, and show good spinnability compared with mesophase pitch.

As understood from Table I, there is some correlation between the mechanical property of carbon fibers and the production process or nature of the precursor. Qualitatively summarizing, we can rather obtain carbon

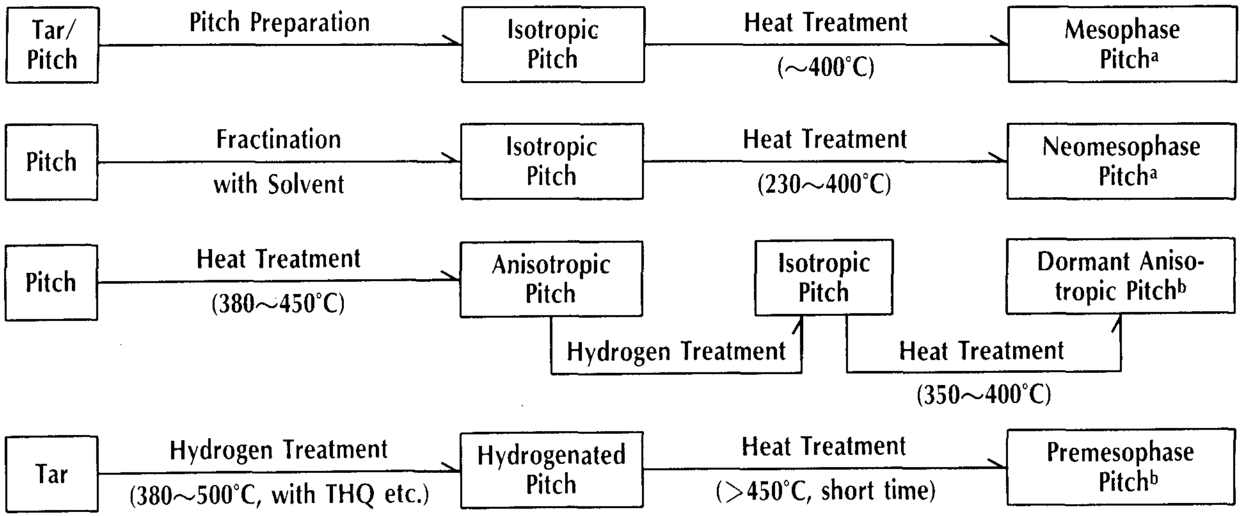


Fig. 2 Typical preparation methods of precursor pitch for high performance carbon fiber

a: optically anisotropic

b: optically isotropic

fibers having higher strength from PAN precursor. This tendency is due probably to non-graphitizable nature and a suitable superstructure of the precursor fiber. While pitch precursor tends to give higher modulus of elasticity, which originates in that pitch is intrinsically converted to soft-carbon.

After activated carbon fiber derived from rayon, several products made from various kinds of precursors including PAN and pitch came into the market[15)~17)]. They are different in surface property, in other words, the adsorption performance as well as cost, as seen in Table I.

The invention of the seeding method with ultrafine metallic catalyst particles[18)] and the fluidizing catalyst method[18)] has remarkably advanced the production technology of vapor-phase-grown carbon fibers, which are still under development.

4. Existing Application Situation

Carbon fibers are used in almost all industries and most of the fibers are used as reinforcements for composite materials, as seen in Table II, where the application fields and related industries which use or will use products derived from carbon fibers are summarized.

Major application is, at present, resin matrix structural materials with light weight and high rigidity for aircraft, sporting goods etc, while application to construction mate-

Table II Application of Carbon Fibers

PRODUCT		APPLICATION	RELATED INDUSTRIES
FIBER		INSULATING MATERIALS (a)	ELETRONICS, CAR, AIRCRAFT, ATOMIC ENERGY
		SEALING MATERIALS (a, b)	CHEMICAL, PETROCHEMICAL
COMPOSITE	RESIN	FUNCTIONAL MATERIALS (a, b) (tribological, conductive, chemical-resistant materials and so on)	APPLIANCE, ELECTRONICS, COMMUNICATION, MACHINE, CAR, AIRCRAFT, CHEMICAL, MEDICAL
	CARBON	STRUCTURAL MATERIALS (b) (light weight / high rigidity materials)	SPORT, MEDICAL, SPACE, AIRCRAFT, CAR, COMMUNICATION
		ABLATION MATERIALS (a, b)	SPACE, MILITARY
	METAL	FRICTIONAL MATERIALS (a, b)	AIRCRAFT, CAR, RAILWAY, MACHINE
		CARBON / GRAPHITE (a)	STEEL, METAL
		CELL ELECTRODES (a, b)	ELECTRIC POWER, CAR
	INORGANICS	CONSTRUCTION MATERIALS (a, b)	SHIP, BUILDING, HOUSING, PUBLIC WORKS

a : GP GRADE, b : HP GRADE, —— : ACTUAL USE, ······ : DEVELOPMENT rials has been growing in the past several years.

For example, the Voyager aircraft, which achieved a non-stop, unfueled, round-the-world flight in 1986, had a structure weight of 422 Kg, and its take-off weight was 5,153 Kg, some 4,065 of that being fuel, thanks to the use of CFRP for 90% of the aircraft's structure[20].

Although this is an extreme case and it cannot be concluded that CFRP will be immediately applied to primary structure in all kinds of passenger aircraft, we can confidently expect a bright future for the application of CFRP to aircraft, as illustrated in Fig. 3[21], which forecasts that 60% of the structure of passenger aircraft will consist of composite materials.

We can improve brittle hydraulic cement materials by reinforcing with carbon fibers, whose major reinforcing effects are: Remarkable improvement in tensile and flexural strength as seen in Fig. 4, where flexural strength to deflection curves of typical examples of concretes fortified with inorganic and organic fibers are summarized, Drastic increase in toughness and ductility (refer to Fig. 4), Significant improvement against impact force, High dimensional stability, Protection against crack formation due to drying shrinkage, Excellent durability, Good wear resistance, Anti-static charge, Light weight and so on.

Thanks to the above-mentioned advantages of carbon fiber reinforced concrete (CFRC) compared with conventiona precast concretes and other fiber reinforced concrete, CFRC has been

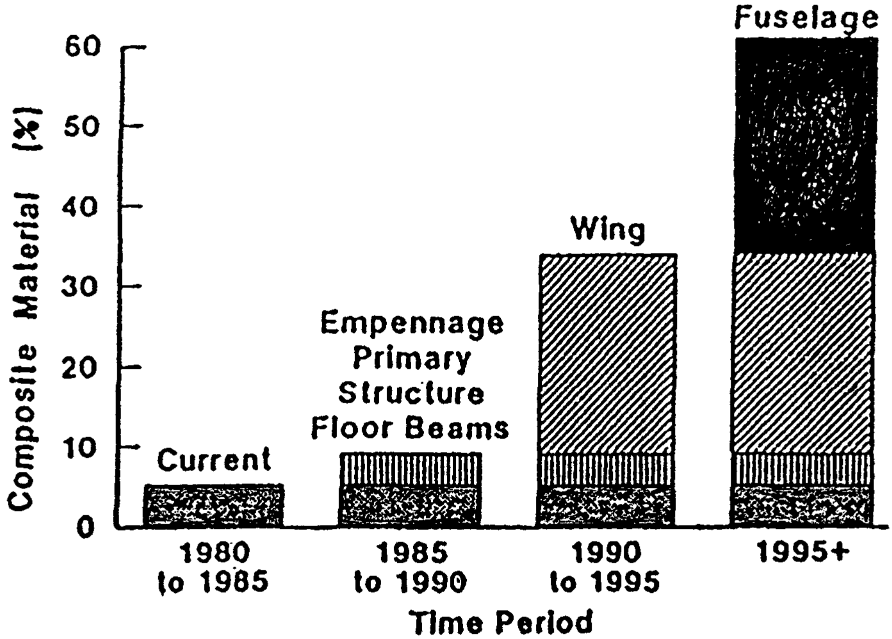


Fig. 3 Future application of composite materials to passenger aircraft [21)]

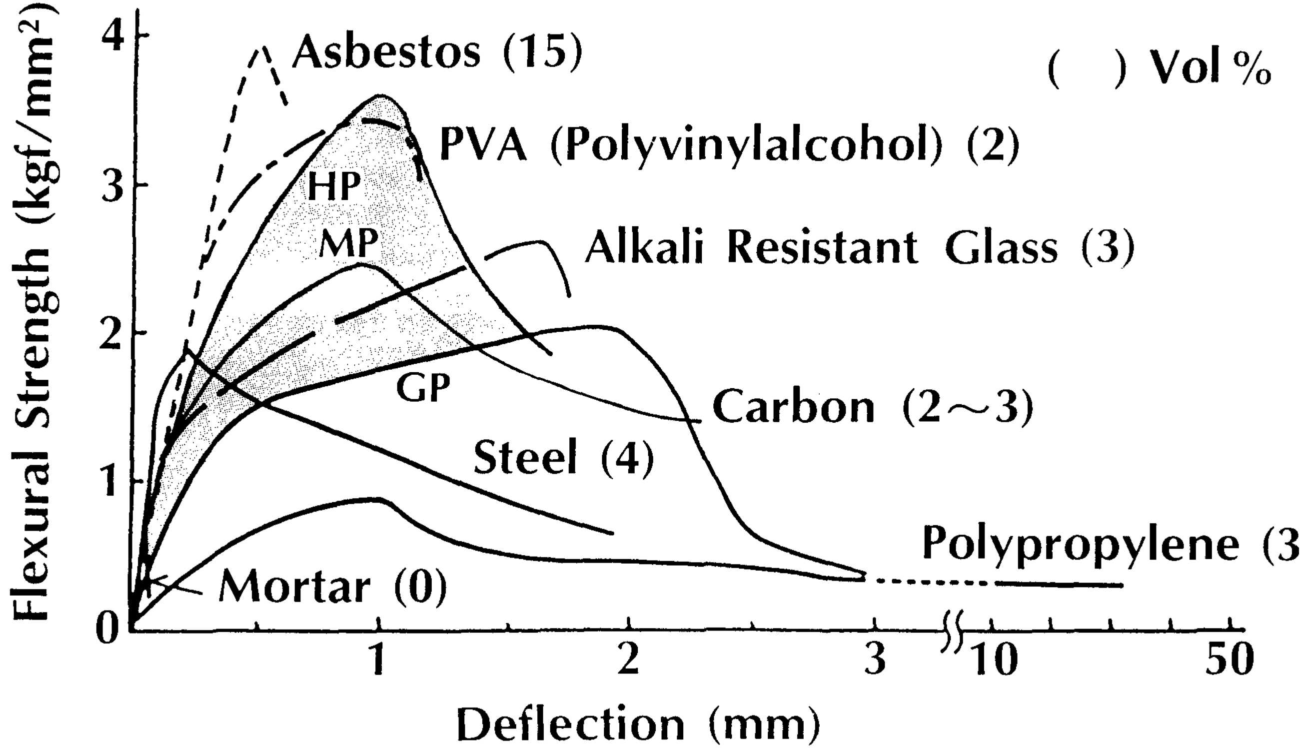


Fig. 4 Flexural properties of fiber-reinforced concrete

utilized for many constructions including the 37-story ARK Building completed in 1986 [22] and is expected to play an important role in the construction industry in the future.

5. Concluding Remarks

The production technology of carbon fibers has been significantly advancing for the past decade, though that of high performance fibers from pitch is still in its infancy. Accordingly, they have gained a position as the leading reinforcements and are used in almost all industries including the aerospace industry. Moreover, they are expected to grow at a rate of 10% or higher in the ACM market for some ten years and also a huge new demand such as for construction materials is confidently expected to be created, presupposing progress in the application technology of carbon fibers for manufacturing composite materials.

REFERENCES

1) R. Bacon, "Carbon Fibers from Rayon Precursors", Chemistry and Physics of Carbon, Vol. 9, p. 1 ~ 102, Edited by P.L. Walker & P.A. Thrower, Marcel Dekker, Inc., New York, 1973.

2) UCC, "Fibrous Graphite", USP 3107152 (1963) etc.

3) UCC, "Process for Producing Fibrous Graphite", USP 3454362 (1969).

4) A. Shindo, "Method for Production of Carbon Products from Acrylonitrile-based Synthetic Polymers", JP S37-4405 (1962).

5) W. Johnson, L.N. Phillips & W. Watt, "The Production of Carbon Fibres", BP 1110791 (1964).

6) Toray, "Production Method for Heat Resistant Polymeric Materials", JP S46-35853 (1971) etc.

7) S. Otani, "On the Carbon Fiber from Molten Pyrolysis Product", Carbon, 3, 31 (1965).

8) Kureha, "Method for Production of Carbon Fibers from Molten Pyrolysis Material", JP S41-15728 (1966) etc. (GP), "Production of Carbon Shaped Articles Having High Anisotropy", JP S49-8634 (1974) (HP).

9) S. Otani, Y. Kokubo & T. Koitabashi, "The Preparation of Highly-oriented Carbon Fiber from Pitch Material", Bull. Chem. Soc. Japan, 43, 3291 ~ 3292 (1970).

10) UCC, "High Modulus, High Strength Carbon Fibers Produced from Mesophase Pitch", USP 4005183 (1977).

11) Toyo Spinning, "Production Method for Fibers Having Adsorption Function", JP S49-133624 (OPI) (1974) etc.

12) du Pont, "Carbonaceous Pitch for Production of Carbon Fibers and Its Production Method", JP S63-5433 (1979 OPI) etc.

13) S. Otani, A. Kikuchi & E. Ota, "A Study on Domant Mesophase Pitch", Meeting of the 117 Committee of

Japan Soc. for the Promotion of Science, 117-163-A-2, Tokyo, 1981.

14) Y. Yamada, "Mesophase Pitch-based Carbon Fiber", Seminar of the Carbon Soc. of Japan, P. 11 ~ 18, Tokyo, 1983.

15) Toho Rayon, "Production Method for Activated Carbon", JP S51-132193 (OPI) (1976) etc.

16) Nippon Kynol, "Production Method for Activated Carbon Fibers or Activated Carbon Fiber Structures", JP S55-7583 (OPI) (1980) etc.

17) Osaka Gas, "Production Method for Carbon Fibers", JP S61-28020 (OPI) (1986) etc.

18) M. Endo, T. Komaki & T. Koyama, "Vapor-grown Carbon Fibers by Seeding Method of Metal Ultra-fine Particles", Interntl. Symp. on Carbon, p. 515 ~ 518, Toyohashi, 1982

19) M. Endo & M. Shikata, "Growth of Vapor-grown Carbon Fiber Using Fluid Ultra-fine particles of Metals", Oyobutsuri, 54, 507 ~ 510 (1985).

20) D. Brewer, "Voyager's Composites 'Performed Superbly'", Adv. Composites, Jan./Feb., 1987, 58 ~ 60.

21) M. Ohsumi, "Aircraft · Space", 87/3rd Joint Meeting of Research Groups, Soc. Polymer Sci., Japan, p. 1 ~ 4, Tokyo, Feb., 1988.

22) S. Akihama, T. Suenage & N. Nakagawa, "Carbon Fiber Reinforced Concrete", Concrete Interntl., 10, No. 1, 40 ~ 47 (1988).