

**ID 1010**

## **DEVELOPMENTS IN HIGH MODULUS FINE FIBRE REINFORCEMENTS FOR COMPOSITE MATERIALS**

A.R.Bunsell

*Ecole des Mines de Paris, Centre des Matériaux, B.P. 87, 91003 Evry Cedex, France*

**SUMMARY:** The development of composite materials has followed closely the development of high modulus fibres which have become available as reinforcements. Improvements of these fibres have been achieved through a better understanding of the relationships between the mechanical properties and the microstructures of the fibres which in turn are controlled by a better understanding of the manufacturing processes. This is true for all classes of fibres whether organic, carbon or ceramic in composition. Fibre reinforcement usually gives enhanced properties when compared to the unreinforced material. The fibres used in composites have been improved continually and in some respects it is likely that their ultimate properties, such as density, temperature and chemical stability and stiffness, have been attained however improvements can be expected to continue in the ultimate strengths of fibres as strength is defect controlled rather than being a fundamental property of the fibre.

**KEYWORDS :** Fibre reinforcements, properties, elastic modulus, high temperature organic, carbon, ceramic

### **INTRODUCTION**

High modulus synthetic fibres are those which show great longitudinal stiffness. Although stiff along the fibre length they are flexible when bent because of their small diameters, which are of the order of 10 microns. Their flexibility, coupled with high Young's moduli, high strengths and low densities make them essential for the development of composite materials. The fibres describe in this paper are for the most part destined for use in high performance composites and an arbitrary lower Young's modulus of 100 GPa has been adopted in defining high modulus although references will be made to some other lower modulus fibres

The development of high modulus synthetic fibres began in the 1930s with the commercial production of glass fibres in the USA. Glass and glass fibres have approximately the Young's modulus and density of aluminium. The first synthetic polymeric fibres were

produced in 1938. These were polyamide (PA)6.6, developed in the USA and PA 6 fibres produced in Germany (Chawla)[1]. These PA, or "nylon" fibres, together with polyester (PET) fibres developed in UK in the 1940s are the most important synthetic textile fibres produced. Although of low stiffness, they were the first of a family of organic fibres which have been developed with elastic moduli rivalling and even exceeding that of steel, but with only a fifth or less of its weight. The highest Young's moduli of commercially available organic fibres is forty percent higher than that of steel. This remarkable behaviour is due to the fibres' molecular structures which make optimum use of the aligned covalent bonds in the molecular backbone. Large diameter (140 $\mu$ m) boron and silicon carbide fibres made by chemical vapour deposition (CVD) onto a filament of tungsten or carbon were first produced in the early 1960s first in the USA and then in France and Russia (Bunsell)[1988]. They have the density of glass but twice the Young's modulus of steel. Control of the surfaces of the SiC fibres allows them to be used as reinforcements for titanium. Carbon fibres, with a density of a quarter that of steel, were first produced in Great Britain in the middle 1960s. They are made by the pyrolysis of polyacrylonitrile (PAN) precursor fibres and commonly have moduli up to one and half times the modulus of steel but can be up to three times stiffer (Kostifkov) [3]. An alternative process developed in the 1970s in the USA uses the pitch residue from oil refining or the coking of coal to give fibres with moduli approaching that of diamond, which defines the maximum stiffness available in nature. Fine ceramic fibres started to appear at the end of the 1970s and in the 1980s. One group of these fibres developed in the UK and in the USA, is based on alumina (Al<sub>2</sub>O<sub>3</sub>) whereas others developed in Japan based on silicon carbide (SiC) (Bunsell and Berger)[4]. The latter fibres can now resist temperatures of up to 1400°C with no change in strength or stiffness and probably represent the optimum form of these fibres for reinforcing ceramic matrices (Bunsell and Berger)[5]. Ceramic fibres have Young's moduli ranging from that of steel to twice this value with densities less than half that of steel.

The fineness of fibres allows even the stiffest of materials to be made in a flexible form as bending stiffness is related to the cube of the diameter. However many high modulus fibres are completely elastic, at least at room temperature, and are therefore brittle. The oriented polymer fibres are not brittle as they deform plastically in compression. They show great toughness which can be exploited in structures which must resist impacts.

## **ORGANIC FIBRES**

Polyamide (PA) fibres are based upon amide groups (-C(O)NH-) contained within a backbone of carbon atoms linked by strong covalent bonds as can be seen from Table 1. However the molecules are linear and can bend and rotate at each bond which results in a low Young's modulus. Table 1 shows that the PET molecule contains an aromatic ring which stiffens it. Interchain linking between the molecules, in both PA and PET fibres, occurs by hydrogen bonding which provides good transverse properties for the fibres. Both PA and PET fibres melt at around 260°C although it is significant that the PET fibre, which contains the aromatic rings, shows much higher resistance to discoloration at raised temperatures. Higher melting points or decomposition temperatures and much higher Young's moduli have been achieved by including more aromatic rings in the molecular main chain and by aligning these very rigid molecules parallel to the fibre axis (Table 1).

Fibre	Repeat Unit in the Macromolecule	Max Elastic Modulus (GPa)
Polyamide 6/6 Nylon 6/6	$-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-$	5
Polyethylene terephthalate [Polyester]	$-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-$	18
Poly-paraphenylene/3,4-diphenylether terephthalamide [Technora]	$\left( \text{HN}-\text{C}_6\text{H}_4-\text{NHOC}-\text{C}_6\text{H}_4-\text{CO} \right)_m \left( \text{HN}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_3-\text{NHOC}-\text{C}_6\text{H}_4-\text{CO} \right)_n$	70
Poly(p-phenylene terephthalamide) [Kevlar]	$-\left[ \text{HN}-\text{C}_6\text{H}_4-\text{NH}-\text{CO}-\text{C}_6\text{H}_4-\text{CO} \right]-$	135
Poly(p-phenylene benzobisoxazole) PBO [Zylon]	$\left[ \text{C}_6\text{H}_4-\text{C}_5\text{H}_2\text{N}_2\text{O}_2 \right]$	280

Table 1 : The molecular structures of organic fibres have become increasingly more complex

The aramid family of fibres are made up of aromatic PA and possess Young's moduli, more than twenty times that of conventional polyamide fibres and twice that of glass (Table 2). This group of fibres, first introduced as the Kevlar fibre from Du Pont, has been available

since 1972. Molecular alignment in these fibres occurs because of the very stiff molecules which are aligned preferentially parallel to the fibre axis by the shear forces induced in the spinning process and held together, in one direction by hydrogen bonds and in the other by Van der Waals' bonds, which are ten times weaker. The structure of aramid fibres is very well ordered, however they are highly anisotropic which results in them being weak in all directions except in tension parallel to the fibre axis and, because of the need to remove the solvent, the fibres contain pores. As a consequence failure of these fibres is nearly always highly fibrillar. In tension Kevlar fibres are five times as strong as steel in air for the same weight. In compression the fibres deform plastically. This results in the fibres being difficult to cut as well as giving great tenacity and resistance to impact loading. Their highly anisotropic behaviour means that the fibres are not used in primary loading structures subjected to compressive forces. Aramid fibres, other than Kevlar, which are commercially available are the Twaron fibre from Acordis in Holland and the Technora fibre from Teijin in Japan. Technora is based on a molecule which is not straight and as a consequence the fibre has an intermediate Young's modulus.

In 1998 a fibre which had been developed in US Air Force laboratories began to be produced commercially, under license, by the Toyobo Company. Its chemical composition is Poly(p-phenylene benzobisoxazole), PBO, and it is produced under the name of Zylon. The producers report that the fibre has remarkable properties, in tension, as can be seen from Table 2. It has a Young's modulus which is twice that of kevlar, since unlike kevlar, the PBO molecule, shown in Table 1, is completely straight thus making the most of the covalent bonds in its structure. This fibre most likely represents the upper practical limit for the Young's modulus of commercial organic fibres. PBO fibres however suffer from poor compressive strength as molecular interchain cohesion is assured by Van der Waals' bonds.

Recently Acordis have announced the development of an experimental fibre which they call M5 and which is said to possess a Young's modulus of 330 Gpa, but above all superior compressive properties as molecular interchain cohesion is ensured by hydrogen bonds. This leads to a slightly higher specific gravity of 1.7. Compressive strength is said to be four times higher than that of the PBO fibres and nearly three times higher than kevlar fibres.

and rigid.

Simple polymers could, if all their molecules were aligned parallel to one another, give materials with the characteristics of high performance materials. Such fibres can be made using polyethylene (PE) dissolved in a solvent to make a very dilute solution which is then spun. Such fibres were first produced in Holland by DSM, in collaboration with Toyobo, under the name Dyneema, and Allied in the USA under the name Spectra. The fibres consist of PE molecules which are aligned parallel to the fibre axis with molecular interchain

cohesion assured by Van der Waals' forces. They have properties in tension rivalling those of the aramid fibres with a lower specific gravity (0.97).

Fibre	Composition	Diam. (µm)	Specific Gravity	Young's Modulus (GPa)	Strength (GPa)	Failure strain (%)
PA 66	PA66	20	1.2	< 5	1	20
Polyester	PET	15	1.38	< 18	0.8	15
Technora	PPDT	12	1.39	70	3	4.4
Kevlar 49	PPTA	12	1.45	135	3	4.5
Zylon	PBO	12	1.56	280	5.8	2.5
PE	PE	38	0.96	117	3	3.5

Table 2 : Comparison of organic fibre properties.

Like all highly oriented organic fibres their properties in compression of PE fibres are poor. These fibres are limited in temperature to a maximum of 120°C as they melt around 150°C and suffer from creep.

## CARBON FIBRES

Carbon is the sixth lightest element and the carbon-carbon covalent bond is the strongest in nature. Many fibres can be converted into carbon fibres, the basic requirement being that the precursor fibre carbonises rather than melts when heated. However most carbon fibres are made by a process developed first in the UK and then in Japan in the late 1960s based on the conversion of acrylic fibres. The properties of carbon fibres made by this route depend on the temperature of pyrolysis. At around 1500°C the strength of the fibres reaches a maximum. Above this temperature the basic carbon structural units increase in size which results in a fall in strength whereas the Young's modulus increases continuously with increasing temperature up to around 3000°C. The structure which results from the pyrolysis of PAN is highly anisotropic, with the basic structural units formed by the carbon atom groups aligned parallel to the fibre axis. Table 3 shows some typical properties of carbon fibres, however there exists a considerable range of properties for these fibres. The earliest and still the most widely used carbon fibres made from PAN were made from similar precursors which gave fibres of 7µm diameter. The range of high strength and high moduli fibres made from these precursors are produced by varying the pyrolysis temperatures. The higher strength fibres are produced by using finer precursors which give carbon fibres of 5µm diameter and which allow higher strengths to be obtained, of up to 6.5GPa. This increase in strength compared to

earlier generation of fibres is accounted for by the probability of finding a defect in the fibre. As the volume of the fibres per unit length is reduced the chances of a significant defect existing in the length is considerably reduced and so the average strength of the fibres increases. The reduction from 7 to 5 $\mu\text{m}$  may seem slight but the cross sections of the fibres was reduced to a half of their former value and so the effect on fibres strength is very significant. Although carbon fibre tensile strength could theoretically be further enhanced such improvements are not accompanied by increases in compressive strength. The higher Young's moduli are obtained by heating to around 3000°C which has considerable cost implications and so probably represents the upper limit of elastic moduli for carbon fibres made from PAN.

Fibre Type	Manufacturer	Trade Mark	Diam. ( $\mu\text{m}$ )	Density ( $\text{g/cm}^3$ )	Strength (GPa)	Strain to failure (%)	Young's Modulus (GPa)
Ex PAN							
High strength	Toray	T400H	7	1.80	4.4	1.8	250
High strength	Toray	T1000	5	1.82	7.1	2.4	294
High Modulus	Toray	M46J	7	1.84	4.2	1.0	436
High Modulus	Toray	M60J	5	1.94	3.92	0.7	588
Ex Pitch							
Oil derived pitch	Nippon Oil	Granoc XN-40	11	2.10	3.7	0.9	390
Oil derived pitch-High Modulus	Nippon Oil	Granoc XN-80	11	2.16	3.5	0.5	780
Coal tar pitch	Mitsubishi Chemicals	Dialead K1352U	10	2.12	3.6	0.58	620
Coal tar pitch	Mitsubishi Chemicals	Dialead K13B2U	10	2.16	3.9	0.48	830

Table 3 : Typical characteristics of carbon fibres

Carbon fibres made from pitch based precursors were developed in the USA in the early 1970s and in Japan in the 1980s. The high carbon yield of pitch which approaches 90 % makes it an attractive and cheap source for making carbon fibre precursors. Cost however is increased by the purification processes by which the pitch is converted into a mesophase or liquid crystal solution which is then spun giving precursor fibres with aligned microstructures. Pitch based precursors heated to around 2300°C give fibres with Young's moduli as high as those obtained with PAN based fibres at 2900°C and heating to these higher temperatures gives even greater stiffness of up to four and a half times that of steel. It is therefore more economical to produce high modulus carbon fibres from pitch than it is from PAN. The properties are due to a less disordered, more graphitic microstructure of the

pitch based fibres which however leads to lower compressive strength and increased costs in producing high strength carbon fibres.

## OXIDE FIBRES

The oxide of aluminium, alumina ( $\text{Al}_2\text{O}_3$ ) is a hard brittle material with excellent refractory properties up to  $1600^\circ\text{C}$ . The atomic structure of this material is assured by a mixture of covalent and ionic bonds. Alumina exists in a range of phases of which the most stable and crystalline form, to which every other phase is converted around  $1200^\circ\text{C}$ , is alpha alumina which has a Young's modulus of around 400GPa. Several manufacturers have produced continuous  $\alpha$ -alumina fibres as can be seen from Table 4. The control of grain growth and porosity in the production of alpha-alumina fibres is difficult so that the different manufacturing routes adopted have produced fibres with different Young's moduli.

Fibre Type	Maker	Trade Mark	Composition (wt %)	Diameter ( $\mu\text{m}$ )	Density ( $\text{g}/\text{cm}^3$ )	Strength (GPa)	Strain to failure (%)	Young's Modulus (GPa)
	Mitsui Mining	Almax	99.9% $\text{Al}_2\text{O}_3$	10	3.6	1.02	0.3	344
	3M	610	99% $\text{Al}_2\text{O}_3$ 0.2%-0.3% $\text{SiO}_2$ 0.4-0.7% $\text{Fe}_2\text{O}_3$	10-12	3.75	1.9	0.5	370
alumina silica fibres	ICI	Saffil	95% $\text{Al}_2\text{O}_3$ 5% $\text{SiO}_2$	1-5	3.2	2	0.67	300
	Sumitomo Chemicals	Altex	85% $\text{Al}_2\text{O}_3$ 15% $\text{SiO}_2$	15	3.2	1.8	0.8	210
	3M	Nextel 312	62% $\text{Al}_2\text{O}_3$ 24% $\text{SiO}_2$ 14% $\text{B}_2\text{O}_3$	10-12 or 8-9	2.7	1.7	1.12	152
	3M	Nextel 440	70% $\text{Al}_2\text{O}_3$ 28% $\text{SiO}_2$ 2% $\text{B}_2\text{O}_3$	10-12	3.05	2.1	1.11	190
	3M	Nextel 720	85% $\text{Al}_2\text{O}_3$ 15% $\text{SiO}_2$	12	3.4	2.1	0.81	260
alumina/zirconia	3M	Nextel 650	89% $\text{Al}_2\text{O}_3$ 10% $\text{ZrO}_2$ 1% $\text{Y}_2\text{O}_3$					

Table 4 : Properties and compositions of alumina based fibres

Fibres of intermediate alumina phases can be produced by the inclusion of silica in the structure. The Young's moduli, around 200GPa, of these fibres are lower compared to that of



pure  $\alpha$ -alumina and they are produced at a lower cost. This, added to easier handling due to their lower stiffness, makes them attractive as reinforcements for aluminium alloys in the temperature range of 300-350°C. Continuous fibres of this type can be woven due to their lower Young's moduli. These fibres resist oxidation at high temperatures but the high diffusion rates of the constituent elements means that they creep and also lose strength above 1000°C.

A series of fibres based on a mullite composition consisting of a ratio of 3 moles of alumina to two of silica has been developed by 3M. Mullite has a complex crystallographic structure which is highly resistant to creep at high temperatures. The Nextel 720 fibre from 3M consists of both  $\alpha$ -alumina and mullite phases. Its Young's modulus is 260 GPa. At high temperatures, above 1000°C and up to 1500°C the microstructure of the Nextel 720 fibre leads to a dramatic reduction in creep rate compared to pure alumina fibres but the fibre surface is particularly reactive to alkaline contamination above 1100°C which leads to a fall of strength (Deleglise et al)[6].

### **SILICON CARBIDE BASED FIBRES**

Fine diameter fibres, based on SiC became available in the early 1980s. They are made by the pyrolysis of organo-silicon precursor filaments based on polycarbosilane, which consists of cycles of six atoms arranged in a similar manner to the diamond structure of  $\beta$ -SiC.

The early Nicalon fibres made by Nippon Carbon and the Tyranno fibres from Ube Industries were made by cross linking the precursor fibres by heating in air which introduced oxygen into the structure. The Tyranno fibres already contained some oxygen as it was introduced with a small amount of titanium into the to control spinning. The presence of the oxygen resulted in the SiC grains, about 2nm in size, which were developed during pyrolysis, being surrounded by an amorphous Si-C-O phase and the fibres had Young's moduli of around 200 GPa. This intergranular phase caused the fibres to creep above 1000°C and its degradation above 1200°C limited their use. Cross-linking of the precursors by electron irradiation eliminated the need for introducing additional oxygen into the precursors. This process gave rise to the Hi-Nicalon fibre which had no significant oxygen rich amorphous phase, but considerable excess free carbon. The grain size of the Hi-Nicalon fibre is around 10 nm and its Young's modulus is around 260 GPa. The fibre is more stable than its predecessors at temperatures above 1000°C although grain growth occurs. Both the Japanese manufacturers and Dow Corning have produced a near stoichiometric SiC fibre by extending the above technology and heating the fibres to temperatures up to 1800°C. The fibres differ

in detail which leads to different ultimate properties, as can be seen in Table 5, but all three have grain sizes greater than 50nm

Fibre Type	Manufacturer	Trade Mark	Comp. (wt %)	Diam. ( $\mu\text{m}$ )	Density ( $\text{g/cm}^3$ )	Strength (GPa)	Failure strain (%)	Young's Modulus (GPa)
	Nippon Carbide	Nicalon NLM 202	56.6% Si 31.7% C 11.7% O	14	2.55	2.0	1.05	190
	Nippon Carbide	Hi-Nicalon	62.4% Si 37.1% C 0.5% O	14	2.74	2.6	1.0	263
Si-C based	Ube Industries	Tyranno Lox-M	54.0% Si 31.6% C 12.4% O 2.0% Ti	8.5	2.37	2.5	1.4	180
	Ube Industries	Tyranno Lox-E	54.8% Si 37.5% C 5.8% O 1.9% Ti	11	2.39	2.9	1.45	199
	Nippon Carbon	Hi-Nicalon S	SiC+O+C	13	3.0	2.5	0.65	375
SiC	Ube Industries	Tyranno SA	SiC+C+O +Al	10	3.0	2.5	0.75	330
	Dow Corning	Sylramic	SiC+TiB <sub>2</sub> +C+O	10	3.1	3.0	0.75	390

Table 6 : Properties and compositions of silicon based fibres

and up to 200nm. This leads to Young's moduli of up to 400 GPa. These fibres retain their properties in short term tests to around 1400°C.

## CONCLUSIONS

A wide range of very different fibres have been developed possessing Young's moduli which are very high when compared with many other conventional materials. Many also have low densities making them attractive engineering materials. A detailed understanding of the relationships between manufacturing processes, microstructures and properties has allowed organic fibres to be produced which exploit the limits of atomic bonds which suggests that the limit for Young's moduli of these fibres is being reached. Carbon fibres are produced with moduli approaching that of the stiffest material nature allows. Fine SiC fibres can now maintain their properties to 1400°C although oxidation is a limitation which perhaps further research on oxide fibres may overcome.

## REFERENCES

1. Chawla, K.K. "Fibrous Materials" Cambridge University Press, Cambridge 1998
2. Bunsell, A.R. "Fibre Reinforcements for Composite Materials" Elsevier, Amsterdam 1988
3. Kostikov, V.I. "Fibre Science and Technology" Chapman & Hall, London 1995
4. Bunsell, A.R. and Berger, M-H., "Fine diameter ceramic fibres" J.European Ceramic Soc., 2000, Vol.20, 2249-2260
5. Bunsell, A.R. and Berger, M-H. "Fine Ceramic Fibers" Marcel Dekker, N.Y 1999.
6. Deleglise, F., Berger, M-H., Jeulin, D. and Bunsell, A.R. Microstructural stability and room temperature mechanical properties of the Nextel 720 fibre" J.European Ceramic Soc., Vol.21, 2001, 569-580