FROM POLYMERS TO POLYMERIC CARBON - A WAY TO SYNTHESIZE A
LARGE VARIETY OF NEW MATERIALS

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Abstract - Polymeric carbon became known during the last years
in form of monolytic bulk material as glassy carbon and carbon
fibres as well as in combination of both as carbon/carbon com-
posites. The paper involves a general review of the nature of
these polymeric carbons as a single element polymer with two-
dimensional polymer units. The chemical viewpoints for the
preparation of these polymeric carbons and their application
in combination with organic polymers are treated in detail.

The present and future application possibilities are discussed
basing on the material capacity, technological difficulties
and economic viewpoints.

INTRODUCTION

Polymeric carbon is made from synthetic polymers. World polymer production a-
mounts more than 40 Mio jato. The polymer production including fibres and ela-
stomeres comprises a fifth of the total volume of the production of chemical
industry throughout the world. All synthetic polymers are made of crude oil
as raw material. Therefore, one has to examine whether this basic raw material
for today's polymers and for special new products made from it, will be avai-
lable in the future which will be characterized by a growing energy crisis.
Or, have we to go back to the metals or ceramic materials instead of to pro-
ceed from organic polymers to the low weight anorganic material "Pure Carbon"?
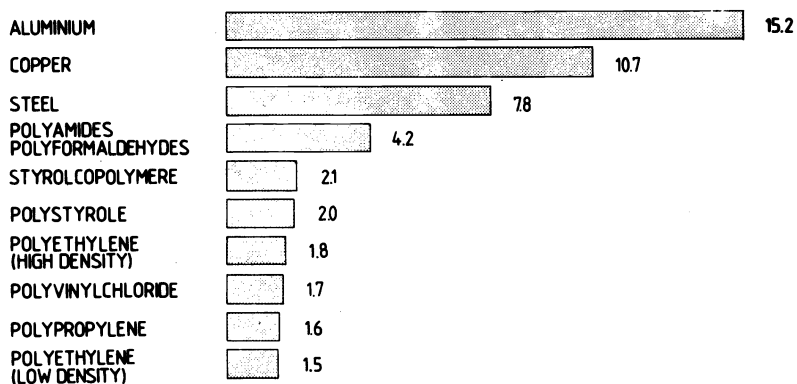

Fig. 1. Oil equivalents for the production of various mate-
rials, needed for energy and raw materials.

Referring to the newest study of chemical industry,Fig. 1 (Ref.1), the need
for energy plus raw material as shown in equivalent units of crude oil is much
lower for polymers than for the most common metals which last ones additio-
nally need other raw materials than oil.

Such comparisons become impressive if we consider the final products for exam-
ple: from 1 kg crude oil 300 m polyethylene pressure water tubes can be pro-
duced, but only 50 m of same sized tubes made of steel with protective coating.
A comparison of waste water tubes shows more than 12 times superiority of PVC
to cast iron. Such considerations became even more impressive if we compare
mobile products for which additional energy is saved during application by
light weight materials (compare Fig.22).

We can conclude that we have not to go back to the metal-age, if we save our fossil fuels as raw material for producing most valuable materials instead of simple burning off.

THE BASIC PROPERTIES OF PURE CARBON AS MATERIAL

The outstanding properties of pure carbon materials if compared with organic polymers are first of all the unlimited thermostability, the high corrosion resistance, and their absolute biocompatibility.

Disadvantages are the poor processibility, and as indirect consequence their poor mechanical properties and their brittle fracture behaviour. Conventional carbon and graphite products must be manufactured like ceramic materials. The heterogeneous structure consists of granular particles and binder bridges with an unavoidable volume fraction of pores in the order of at least 20%. Such a heterogeneous structure does not utilize by far the superiour strength of the chemical bonds between the carbon atoms. For better understanding of the bond strength, we must remember the electron configuration of the carbon atoms in compounds   namely

1) the sp^3 hybridization, resulting in four equivalent uncompletely filled hybride orbitals, and
2) the formation of only three equivalent sp^2 hybrides.

In the last case there remains one original p-orbital which is occupied by the remaining valence electrons. These p-electrons are forming the π -bonds which are weaker than the σ -bonds but contribute to the strength of the three covalent bonds. The total strength of one of these three bonds is 430 kJ/mol, whereas each of the four equivalent bonds in the tetrahydral structure has a strength of 350 kJ/mol only.
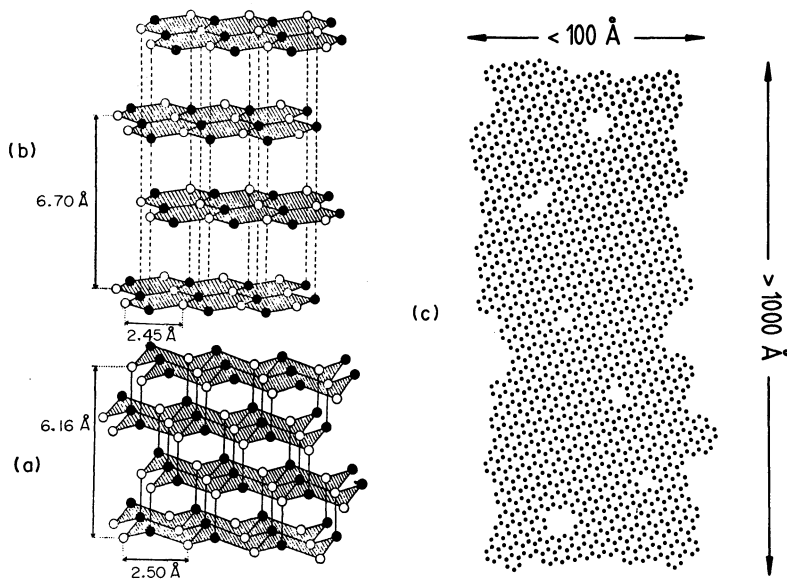

Fig. 2. Structures of elemental carbon :
a) diamond, b) graphite, c) polymeric carbon

Both types of chemical bonds are also found between the atoms of elemental carbon. The sp^3 hybridization in the diamond modification (Fig.2a) and the sp^2 hybridization in the graphite structure (Fig.2b), but also in the imperfect graphitic carbons consisting of layers of different sizes with more or less distortion (Fig. 2c). Typical for these two alternative hybridizations are the different bond angles of 120°C for sp^2 and 109° for sp^3, as well as the different bond lengths and lattice distances. All bonds are strictly orientated. The p_z-orbitals of the sp^2 hybridization are oriented perpendicular to the layer planes. In the perfect graphite lattice however, the wave function of these p-electrons is more extended in space and not localized between two atoms only. This causes mobility of the valence electrons like that in the most metallically bonded elements.

A very weak bond in c-direction of the graphite structure is the consequence. In disordered graphitic carbons, some cross-linking between the layers and limited delocalization of the p-electron is observed.

THE NATURE OF POLYMERIC CARBON

It was known since many years that also structurally disordered carbons, for-
merly defined as "amorphous carbon", consists already of small units of gra-
phitic layers, however, without any crystalline order in the third dimension.
What was not known, however, is the new finding that there exist disordered
carbons which have structural polyaromatic units of strip- or ribbonlike shape
and which are much larger than indicated by wide angle X-ray diffraction mea-
surements. As shown in Fig. 2c, such planar macromolecules are extended up to
100 Å in width, corresponding to a sequence of at about 80 carbon atoms, but
are practically infinitive in length. Only the technique of high resolution
electron transmission microscopy has revealed the structural arrangement of
the ribbons and plates. This molecular structure reminds of the organic poly-
mers with the only difference that not chain- or ladder-molecules but planar
molecules are the structural units. This form of carbon should therefore be
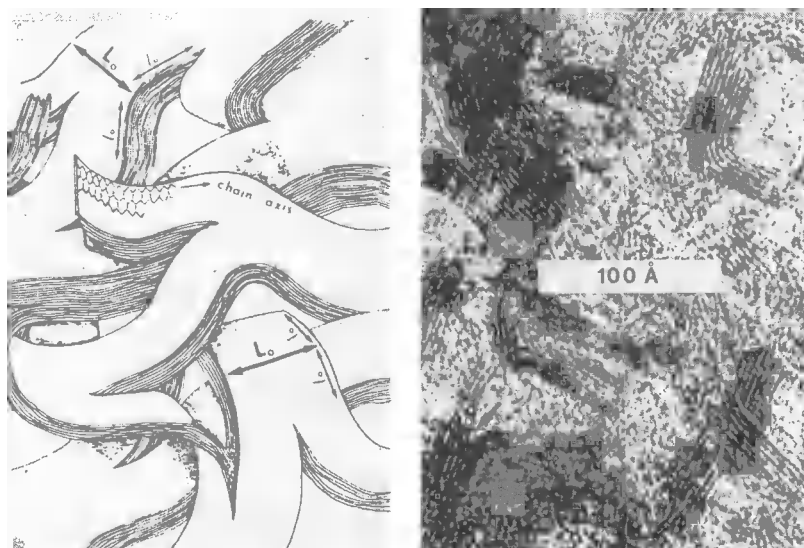named "Polymeric Carbon" (Ref. 2).

Fig. 3. Structural model of polymeric carbon (left)
based on high resolution TEM (right) (Ref. 4).

In polymeric carbons also some of such polyaromatic layers are arranged in pa-
rallel positions but without forming a defined lattice in respect to the
third dimension. The polyaromatics are imperfect themselves. There exists a
strong linkage between the layers, and also some cross linkage between the
plates or ribbons formed by these parallel arranged polyaromatic layers. There-
fore polymeric carbon can not be transformed into a graphite structure by heat
treatment above 2600 °C. It is a so-called "non-graphitizing carbon", that
means the p-electrons are not delocalized and even sp^3 - hybridization can be
assumed in the cross linkages between the polyaromatic molecules. But never,
tetrahydral structure units have been confirmed by X-ray diffraction so far (Ref.3).

The structural model of isotropic polymeric carbon as shown in Fig.3 (Ref.4)
has been developed by TEM studies, but is also supported by improved X-ray -
diffraction and adsorption measurements (Ref. 5).

As far as the realization of bond strength in a bulk material is concerned, we
can expect that the two-dimensional strength within the sheets is distributed
statistically within an isotropic bulk material. If we exclude plastic deforma-
bility, high strength but brittle fracture behaviour should be observed. Such
an isotropic material became known 20 years ago as "glassy or vitreous carbon".
It is made from polyfurfuryl alcohol or phenolics by careful coking. Due to
the analogy with the morphology of the precursor polymer, polymeric carbon
is a monolytic carbon without any grain boundaries. As shown in Fig. 4 the
strength of such isotropic monolytic carbon materials exceeds with 200 MN/m^2
considerably that of conventional polygranular graphites. Only newer types of
ultrafine grained graphite exhibit comparable strength properties.

The striking effect of strength increase was achieved by preferred orienta-
tion of the planar polymeric molecules. As shown in Fig. 4 tensile strength
up to 4000 MN/m² can be obtained in direction parallel with the layers. This
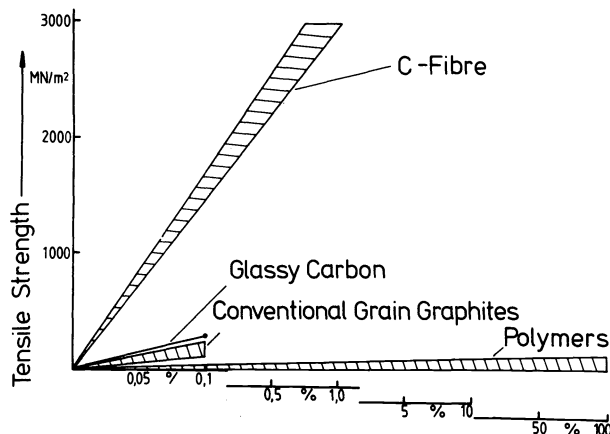second type of monolytic polymeric carbon is realized in carbon fibres.

Fig. 4. Stress/strain-behaviour of various carbon materials

For better understanding table 1 shows where the polymeric carbons are located
within the variety of carbon and graphite materials. We can distinguish bet-
ween fine dispersed carbons (the carbon blacks), the granular carbons (the
electrodes made by a ceramic like process), and the monolytic carbons.

TABLE 1. Variety of carbon- and graphite materials

Besides of the above mentioned polymeric carbons, monolytic carbon can also be
prepared by chemical vapour deposition (pyrolytic graphite). It is discussed
later that carbon fibres can be imbedded in a carbon isotropic matrix like
glassy carbon. Such heterogeneous structure is known as carbon fibre rein-
forced carbon (CFRC), or simply carbon/carbon composites (CCC).

Table 2 (Ref.6) gives a survey on the properties which can be achieved with
the various types of structural carbons and especially on the yield of theo-
retical mechanical properties in solid carbon. The yield of theoretical
YOUNG's modulus is derived from calculations of the bond strength. The aniso-
tropic type of monolytic carbons can achieve up to 50 % yield of the theore-
tical YOUNG's modulus. The estimation of a theoretical strength is based on
the assumption that fracture does not start from cracks but occur simulta-
neously between all atoms of two neighbouring layers. For graphite the maxi-
mum theoretical strength is at about 1:10 of the YOUNG's modulus in a first
approximation.

TABLE 2. Yield of theoretical mechanical properties in the various all-carbon materials

| | MONOLITHIC CARBON | | | HETEROGENOUS CARBON | |
	GLASS LIKE	PYROLITIC	C-FIBRE	C/C-COMPOSITE	POLYGRANULAR CARBON — ultra fine grained type / coarse grained needle type
YOUNGs MODULUS GN/m^{-2}	// 30 ⊥	// 30	//300-500	400	10-12
TENS/FLEX STRENGTH MN/m^{-2}	// 120 ⊥	// 150	//2000-4000	1000	10-80
COMPRESSIVE STRENGTH MN/m^{-2}	// 350 ⊥	⊥ 450			50-200
YIELD OF THEORETICAL YOUNGs MODULUS	// <3 % ⊥	// <5 %	// 30-50 %	50%	<0,2 %
YIELD OF THEORETICAL STRENGTH RELATED TO EXPERIMENTAL YOUNGs MODULUS	< 2,5 %	< 5 %	~10 %	5 %	<0,1 %
(TO THEORETICAL YOUNGs MODULUS)	(0,075%)	(0,1%)	(3-5%)	(2%)	(0,002%)

THE PREPARATION OF POLYMERIC CARBON BY CONTROLLED THERMAL DEGRADATION OF SYNTHETIC POLYMERS

If one takes a natural polymer like wood or jute fibres or coconut shells, the thermal degradation will result in a porous carbon material, in which the cellular structure of the precursor is completely preserved.
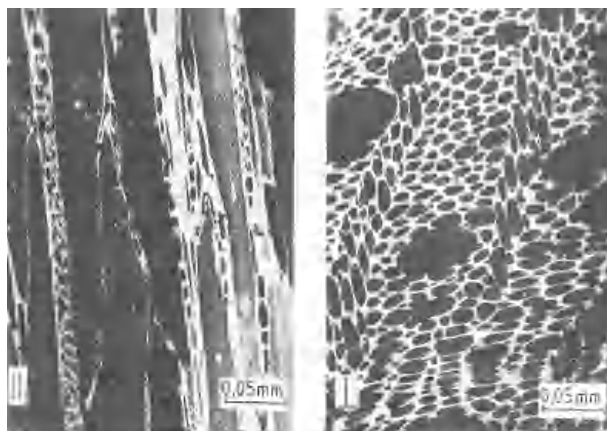

Fig. 5. Optical micrographs of wood-char

Fig. 5 shows the micrographs of a wood char in cross section parallel with and perpendicular to the wood structure. One recognizes by this very porous structure that the structural reorganization of the carbon atoms remaining after carbonization can be realized only in limited areas which have existed before as macro-homogeneous polymer-structures. In the cellulose structure, e.g., these limited areas are fibrillous (Ref. 7). In the case of wood these are the walls of the cells.

The mass loss by volatile byproducts causes a considerable shrinkage. This is easy to understand from the formula of cellulose, and a comparison with the structural arrangement within polyaromatic planes, present in the carbon residue (Fig. 6). The low carbon yield of less than 30 % and the porous structure cause extreme fragility. The mechanical properties can be improved by use of porefree semi-synthetic polymers as precursor, f.i. rayon. Rayon was the raw material for the first carbon fibres in the sixties (Ref. 8), and is still used as raw material for commercially available carbon felt.
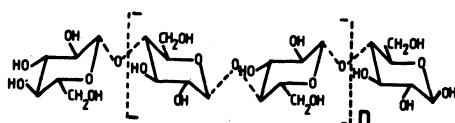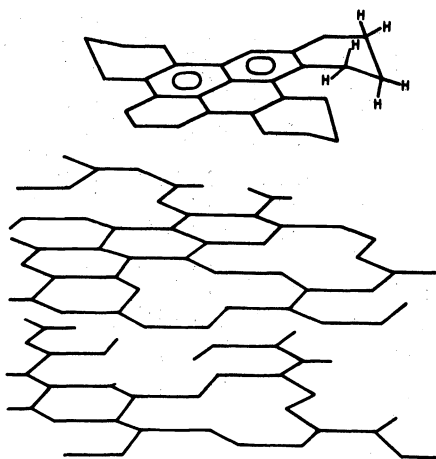
Fig. 6. Structural rearrangement of the C-atoms during pyroly-
sis of cellulose
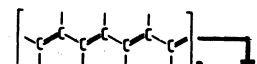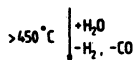Fig. 7. Formation of polymeric carbon from polyfurfuryl alco-
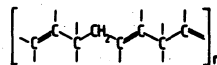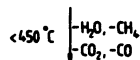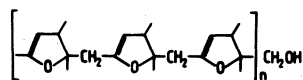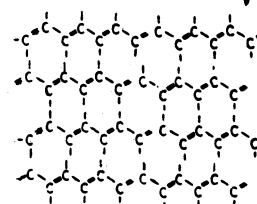hol (Ref. 10,11)

The mechanical properties of carbon fibres from rayon are some orders of mag-
nitude higher than the very first extremely brittle carbon fibres produced
by EDISON, 100 years ago, to be used in electrical bulbs, although at that
time already some hundred thousands of gold dollars have been spent for fin-
ding a better suitable natural precursor material.

A much more perfect formation of the planar, polyaromatic macromolecules which
form the polymeric carbon is achieved by use of thermosetting resins as precur-
sor. In this way a carbon yield up to 50 % and more can be achieved. A linear
shrinkage up to 25 % is reported for polyfurfurylalchohol and for phenolics
as raw material (Ref. 9). The pyrolysis chemistry of polyfurfurylalcohol and
the formation of the carbon sheets out of it are shown in Fig. 7. Most of non-
carbon atoms are splitted off below 450 °C as volatile byproducts (Ref.10).
Above this temperature a high amount of shrinkage is observed. Very carefull
and highly sophisticated X-ray diffraction studies (Ref.11) have shown how
the planar polyaromatic sheets are formed by polymerization reactions from
the linear carbon chains as intermediates. It is assumed that the growth of
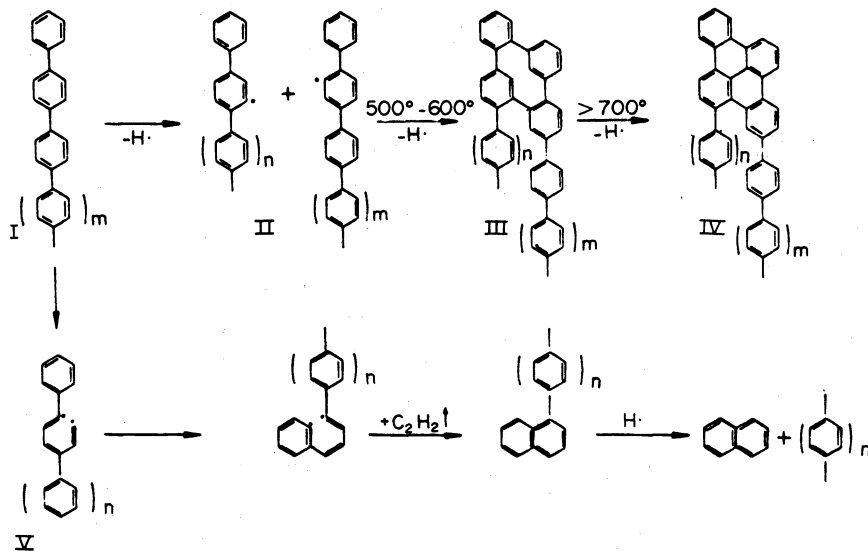these carbon chains controlls the length of the carbon ribbons.

Fig. 8. Thermal degredation of p-polyphenylene (Ref. 12)

From chemical viewpoint p-polyphenylene would be an ideal precursor for poly-
meric carbon because of its high carbon yield of more than 80 % during ther-
mal degradation.
The carbonization chemistry (Fig.8) is so interesting because one can detect
the defect structure of the sheets between 600 and 700 °C by the isolated hy-
drogen atoms in infrared spectroscopy (Ref. 12). Furthermore, one recognizes
that even preformed aromatic rings are splitted off in case of steric hinde-
ring. The practical application of parapolyphenylene as precursor, however,
is limited because of its poor processability. This polymer is non-melting
and also insoluble in all solvents.

A modification of the polyphenylene structure by isomerics (Ref.13) results
in synthetic pitches with lowered carbon yield. Also the precondition of un-
meltability of the polymers is lost, and an additional stabilization treat-
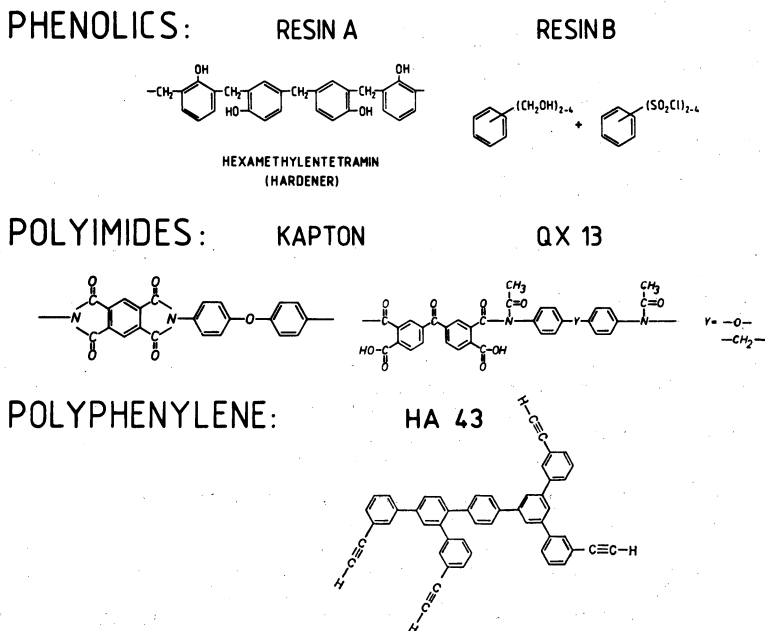ment is needed before carbonization.

Fig. 9. Suitable polymers for the formation of isotropic
polymeric carbon.

Some of the most suitable thermosetting polymers which have been studied as
precursor for polymeric carbon are summarized in Fig.9. Besides phenolics
with various hardeners also polyimides, f.i. "kaptone" foils can be used for
fabrication of polymeric carbon sheets (Ref. 14). The thermosetting resin
HA 43 yields 85 % carbon, because it has a polyphenylene structure. It is cured
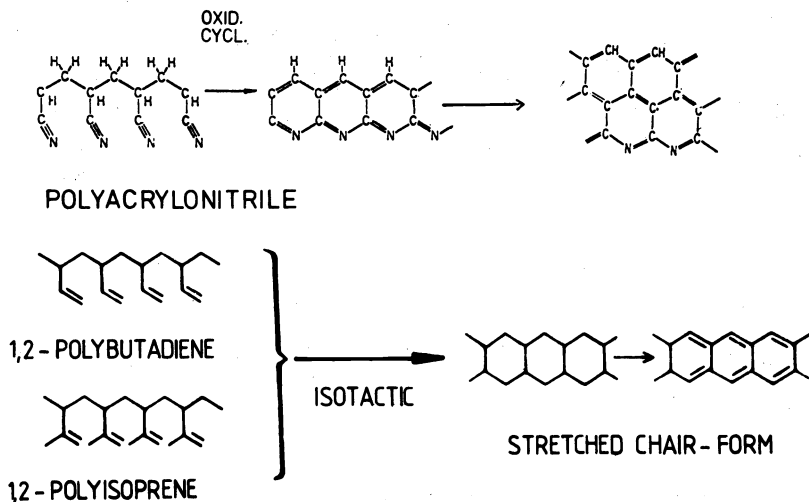by its endstanding acethylene groups (Ref. 15).

Fig. 10. Stabilization of thermoplastic polymer fibres

Instead of using the cross linked thermosetting polymers as precursor material
one can also start from thermoplastic chain-polymers in order to achieve a
better forming into the desired shape, but has to transform the polymer after-
words into a thermostable ladder polymer. This procedure is applied in modern
carbon fibre technology by the so-called stabilization treatment. Best known
is the polyacrylonitrile precursor (PAN) with a continous carbon/carbon
chain as backbone. PAN is stabilized by oxidation treatment in the 200 ^{O}C -
area to heterocyclic naphthyridine ring systems which are dehydrogenated by
oxygene into an aromatic ladder structure (Fig. 10). The planar polyaromatic
polymers are formed by condensation reactions and splitting off the hetero-
atom nitrogen in the temperature range at about 600 ^{O}C. Other chain polymers
like 1,2-poly-butadien or poly-isoprene should react in the same manner, but
are less economic than PAN.

The stabilization treatment is the slowest and thus rate controlling step in
the carbon fibre production because the needed oxygen must diffuse through
the already stabilized outer layer. Therefore, much work has been performed
on the catalysis of cyclization (Ref.16) and on the effect of copolymers
during the stabilization treatment (Ref. 17).

Recently, it was shown that COURTELLE fibres containing 6 % polymethylacrv-
late as co-polymer show a much higher stabilization rate as ORLON which has the
same copolymer (Ref. 18). The high stabilization activity is devoted to an
additional small content of itaconic acid as dying additive in COURTELLE.
If however a prestabilization of ORLON is performed by heat treatment in va-
cuum, the same final oxidation rate as in COURTELLE can be observed, showing
that mainly the outer oxidized shell reduces the stabilization rate.

At the moment it seems that nearly most of commercially available textile
polyacrylo nitrile fibres can be used as precursor for the carbon fibre fabri-
cation (Ref. 19). Only the optimum stabilization conditions have to be modi-
fied. As textile grade PAN fibres are unexpensive the use of petrol pitch as
precursor for carbon fibres due to economic reasons becomes a less attractive
alternative. In any case, the morphology of the precursor fibre is fully
preserved. This can be seen in the micrographs (Fig. 11) for the case of
rayon (left hand side). wet spun PAN (middle part) and for PAN produced in a
dry spinning process (right part)

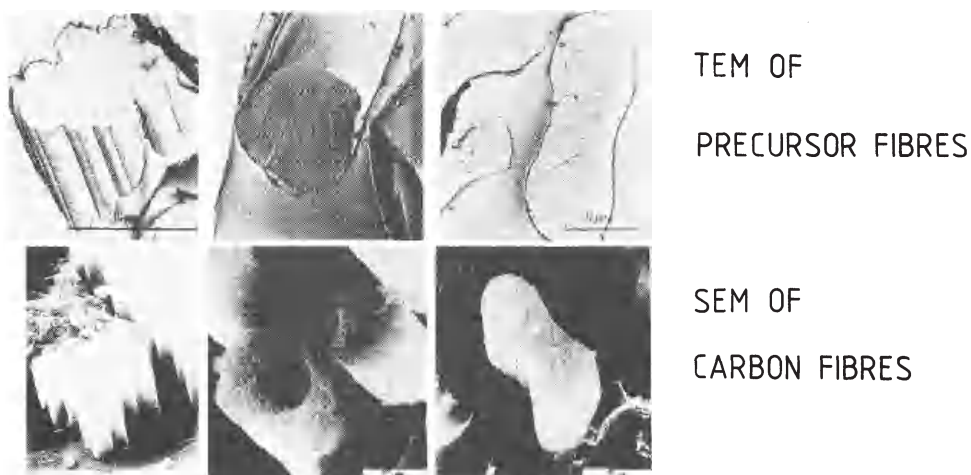TEM OF

PRECURSOR FIBRES

SEM OF

CARBON FIBRES

Fig. 11. Morphology of precursor and carbon fibres (left
rayon, middle part wet spun PAN right part dry spun PAN)

Fig. 12 shows the structural model of anisotropic polymeric carbon from PAN
(Ref.20). The polyaromatic carbon sheets in form of ribbons and plates are
well oriented in the direction parallel with the fibre axes, but do not exhi-
bit a preferred orientation perpendicular to it, so leading to a good com-
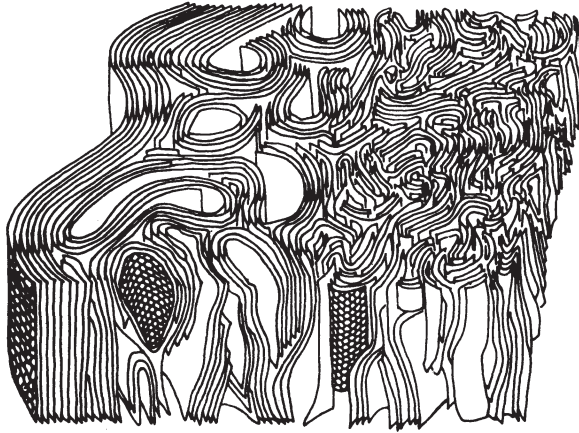pressive strength and sufficient resistivity against shear.

Fig. 12. Structural model of C-fibres prepared from PAN(Ref.2o)

The formation of carbon fibres from pitch follows a different route from che-
mical as well as morphological viewpoint. Pitches form during heat treatment
at 400 °C liquid crystals, a spherical mesophase (Fig. 13),(Ref. 21), which
consists of planar polyaromatics as indicated in Fig. 14 (Ref. 22).

50μm

Fig. 13. Anisotropic mesophase, formed in isotropic petrol
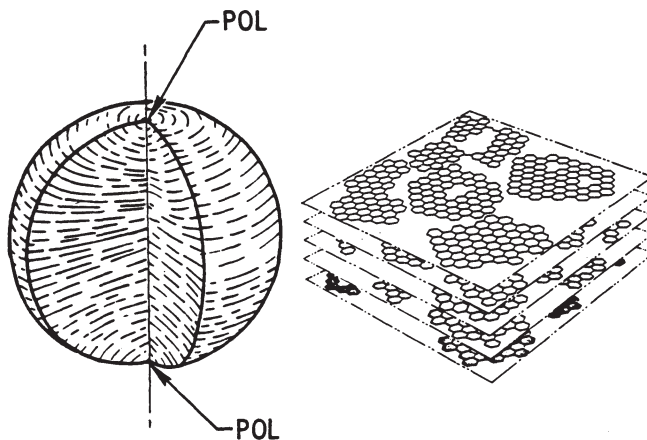pitch by heat treatment at 400 °C.

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Fig. 14. Structural model of the liquid crystal-like mesophase
which consists of planar polyaromatic molecules (Ref. 22).

The mesophase can coalescent, causing an increase of the viscosity, and final-
ly formation of the anisotropic bulk-mesophase which is known to be the star-
ting material for highly anisotropic and well graphitizing coke. If used for
the fabrication of polymeric carbon in the form of carbon fibres it has to be
stabilized after spinning by similar oxidation treatments as PAN, in order to
perform a cross linkage between the planar sheets and to inhibit graphitiza-
tion. The carbon fibres derived from pitch have a different structure and
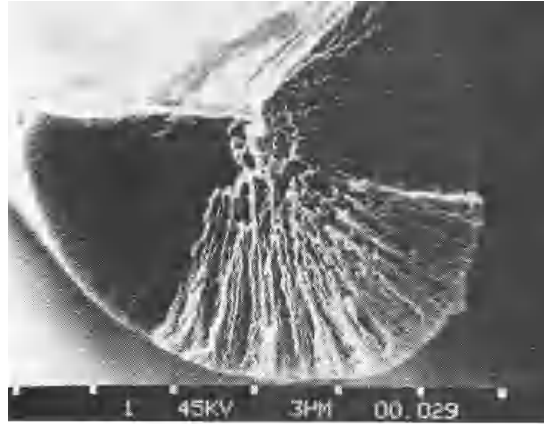thus also different properties (Fig. 15).

Fig. 15. SEM of the fracture surface of a pitch carbon fibre

More important are the final mechanical properties of the various carbon
fibre types. The PAN based carbon fibres are higher in strength, but the
strength decreases by graphitization from 4000 $\rightarrow$ 2500 MN/m^2, whereas the
YOUNG's modulus increases from 250 $\rightarrow$ 400 GN/m^2. The pitch fibres have a lower
strength of 200 MN/m^2 only which is not affected by graphitization treatment.
However, the YOUNG's modulus can increase more by graphitization than in PAN
based carbon fibres, namely from 350   500 GN/m^2.
Tensile strength and YOUNG's modulus of the various reinforcing fibres are
compiled in Fig.16. All C-fibre types exceed the organic high modulus fibres
as far as the YOUNG's modulus is concerned, but only the type II which is
finally heat treated below 1500 $^\circ$C, reaches the high strength of glass and
B-fibres. C-fibres type I are graphitized above 2500 $^\circ$C, those of type III
heat treated below 1200 $^\circ$C only.

The graphitized C-pitch fibres are the best in YOUNG's modulus but lowest in
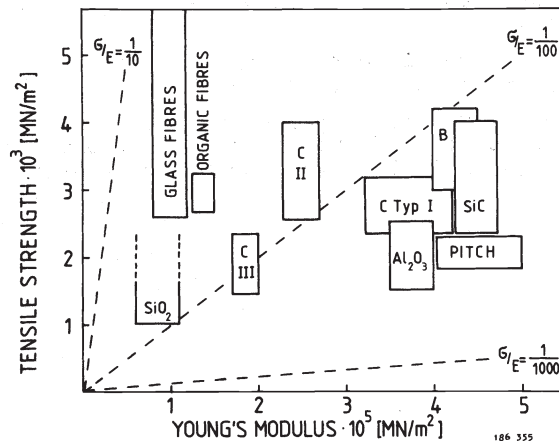strength.

Fig. 16. Tensile strength and YOUNG's modulus of the various
fibres used for reinforcement.

Fig. 17 shows average prices of the various fibres and also the cost of a vo-
lume unit strength and YOUNG's modulus for comparison (Ref. 23). As can be
seen, the organic high modulus- and the glass fibres are the most unexpensive
ones as far as the strength is concerned. Although also the cost for a
YOUNG's modulus volume unit seems to be unexpensive, these fibres are not
suitable for the fabrication of high modulus composites.

The strength unit of PAN-C fibres type II are quite unexpensive, whereas the
even less expensive pitch carbon fibres result in higher costs for the volume
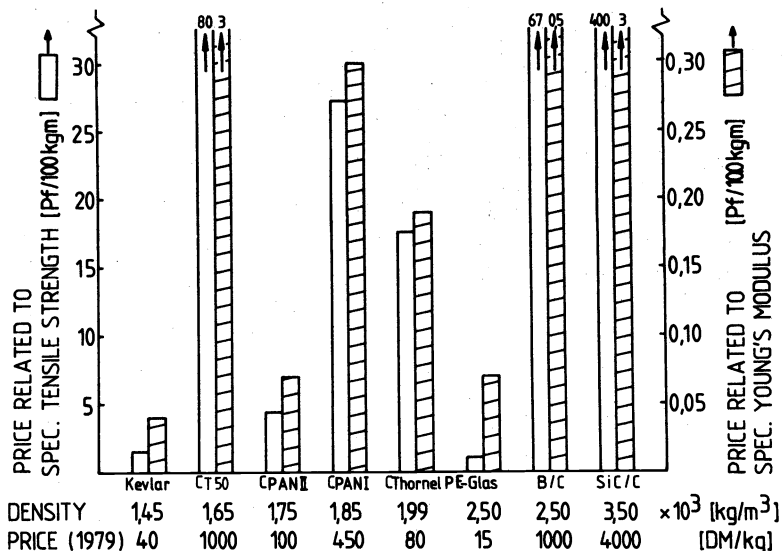unit of strength. This type seems to be advantageous in high modulus struc-
tures only.

		Kevlar	CT50	CPANI	CPANI	CThornel	PE-Glas	B/C	SiC/C	
DENSITY		1,45	1,65	1,75	1,85	1,99	2,50	2,50	3,50	× 10³ [kg/m³]
PRICE (1979)		40	1000	100	450	80	15	1000	4000	[DM/kg]

Fig. 17. Prices of the various fibre types and cost of a vo-
lume unit strength and modulus (Ref. 23).

APPLICATION OF POLYMERIC CARBON AS MONOLYTHIC MATERIAL

The isotropic form of polymeric carbon, the glassy carbon, is a corrosion re-
sistant impervious material with a density of 1,5 kg/m³. The sample sizes
which can be made are limited to some millimeters in thickness due to the ir-
reversible shrinkage during thermal degradation.

This material is used in laboratory equipments, but mainly in human medicine
because of its outstanding biocompatibility, f.i. as electrodes, percutanous
leads, orologic protheses, dental and joint implants. The most striking
success of monolythic carbon is achieved with its application as heart valve
components, where glassy carbon is introduced instead of pyrocarbon for eco-
nomic reasons (Ref. 24).

The anisotropic form of polymeric carbon, the fibres, can be applied for re-
placement of ligands and tendons (Fig. 18, Ref.25, 26).

Following some years of successful experiments with animals, this implanta-
tion technique begins to be transferred to human surgery. There is the possi-
bility even to replace the abdominal wall by carbon fibres in form of waven
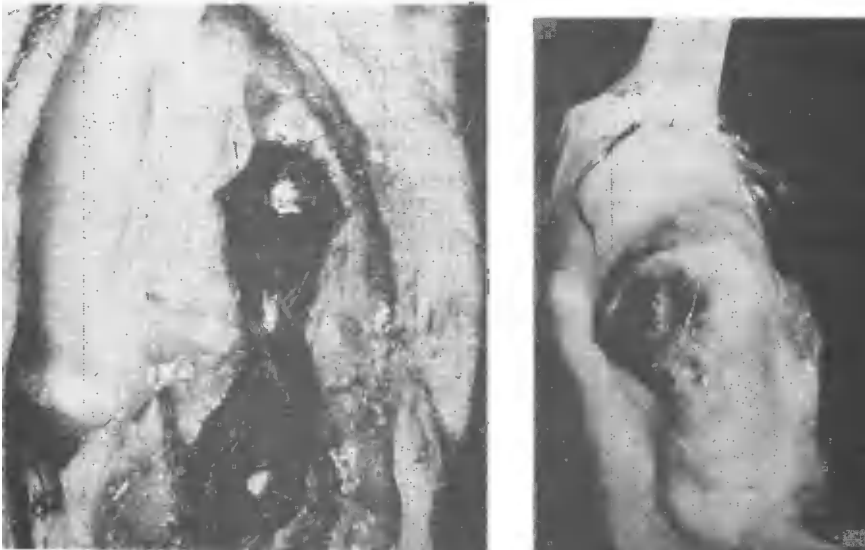textiles (Ref. 27).

Fig. 18. New ligand tissue is grown surrounding the implanted
carbon fibres (Ref. 24).

APPLICATION OF CARBON FIBRES FOR REINFORCEMENET OF POLYMERS

The most important application of anisotropic polymeric carbon is that rein-
forcing fibres in composites, but only some of the most important facts can
be referred in this introductory paper.

A fundamental parameter which controls the final properties of the composite
is the geometric arrangement of the reinforcing fibres within the polymer
matrix. Fig. 19 (Ref.28) shows the effect of the fibre direction on the
strength of the composite for the case of a two-directional reinforcement.
The precalculation is based on a modified rule of mixture, taking into consi-
deration volume fractions and mechanical properties of the components as well
as the direction of fibre arrangement.

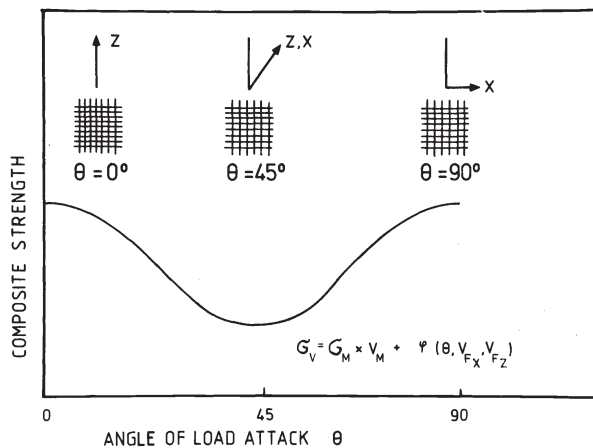$$G_V = G_M \times V_M + \varphi\,(\theta, V_{F_X}, V_{F_Z})$$

Fig. 19. Composite strength for two-directional reinforce-
ment (Ref. 28).

The degree of adhesion between fibre and matrix is another important parameter
which controls the mechanical behaviour of the composite. We have been able
to show that this adhesion is mainly caused by chemical bonds between the
fibre surface and the matrix (Ref. 29). The reactive surface groups on the
carbon fibres play a dominant role for this chemical bonds. If one uses a
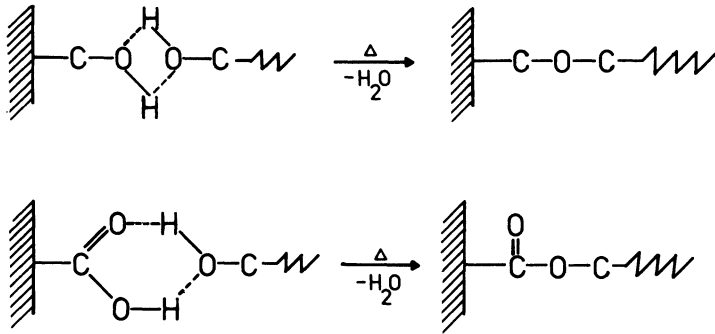surface treated fibre which has been oxidized,various types of surface oxides
are present.

Fig. 20. Chemical reactions between the acid surface groups on
oxidized C-fibres and the hydroxil groups of the phenolic matrix
(Ref. 29).

Fig. 20 for instance shows the chemical reactions between carboxilic groups
on the fibre surface and the hydroxil groups of the phenolic matrix (Ref.29).
Similar reactions are known between acid and basic surface groups on C-fibres
and epoxy matrix (Ref. 30, 31).

Finally, the fracture behaviour of the matrix material is of great impor -
tance. Fig. 21 indicates the stress/strain behaviour for ductile and for
brittle matrices. Full utilization of the fibre strength can only be ob-
tained if the strain to failure of the matrix exceeds that of the fibre
(left part of Fig. 21). Otherwise, the ultimate strength of the composite
will be controlled by the strain to failure of the matrix as indicated in the
right part of Fig. 21. In such cases, fibres with highest YOUNG's modulus are
most advantageous (Ref. 32). This situation will be described with carbon/
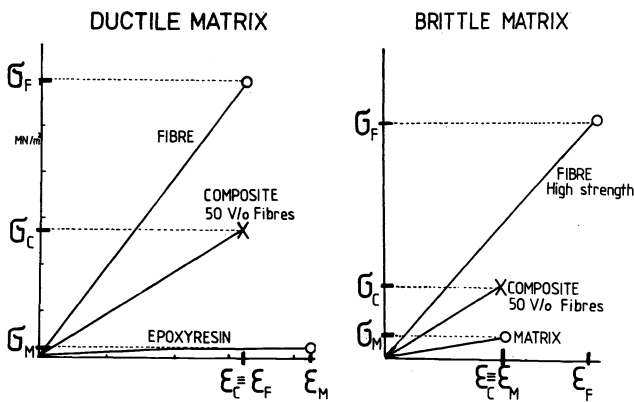carbon composites.

Fig. 21. Stress-strain behaviour of fibre reinforced composi-
tes with ductile and brittle matrix respectively (Ref.32).

The most important applications are C-fibre reinforced polymers. These com-
posites which correspond to the combination brittle fibre with ductile ma-
trix, were introduced into the modern technology by the need of supersonic
aircrafts and space vehicles for extremely stiff but very light new materials
for structures. At the moment an additional tendency to replace conventional
metal parts by such composites in motive structures like cars can be observed
in order to save weight and energy. The car industry in the western countries
try to use fibre reinforced composites in the body structure, frame doors,
front end assembly, drive shaft, bumper, wheels, springs, brakes and other
parts. Even inner parts of the engine can be replaced by composites (33).More
than 5o kg carbon fibres could be used in each car. It was calculated that a

considerable amount of energy can be saved not only during the fabrication, but even more during the use of the car by less fuel consumption, if metals are replaced by carbon/epoxy composites. Figure 22 (Ref.34) shows the results of such precalculations for a 5 year life time of the components.
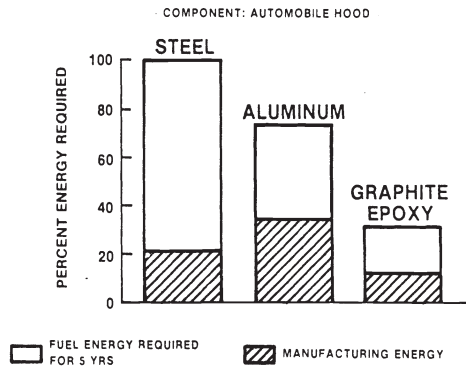

Fig. 22 . Component life time energy savings with composites, replacing metals in future cars (Ref. 34).

There remains no doubt, that carbon fibre reinforced polymers (CFRP) with their extremely high stiffness (up to 30 GN/m^2) and low density (1,5 kg/m^3) will replace metals in the most future applications where weight saving is the main goal. The problem is only that manufacturing of f.i.cars from metals is so highly rationalized in industrialized countries, whereas the present production methods of composites still causes high labour costs. The composite technology offers therefore a great chance for development countries with high labour capacity.
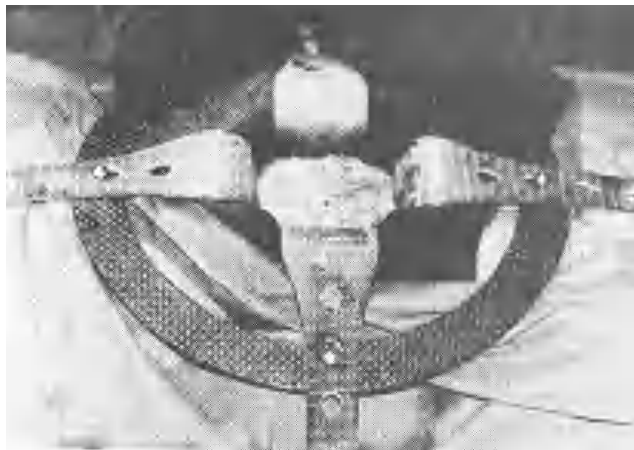

Fig. 23. Surgery tool made of CFRP offers in situ X-ray control during operation.

Also in human surgery, C-fibre reinforced composites will play an important role in future. Bone plates in osteosynthesis are one example (Ref. 35) because of the possibility to tailor the mechanical properties and thus to match the special need controlled by the elastic behaviour of bones. In case of CFRP as material for tools in surgery as shown in Fig. 23 (Ref. 36) one utilizes the additional advantage that neither carbon nor polymers absorbe X-rays and improved X-ray images can be taken in situ during operation.

Recently, other forms of reinforcing elements made of polymeric carbon have been developed, namely the hollow fibres (Ref. 37). Some precalculations of stiffness characteristics of composites with hollow fibres are compiled in Fig. 24 (Ref.38), and one recognizes that the lowered bulk density especially increases the bonding stiffness and the plate buckling strength, properties which offer not only further weight savings, but also improvement and simplification in design and manufacture of airplane structures.
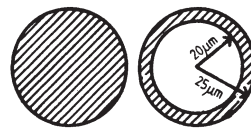
STIFFNESS CHARACTERISTICS:

1. Extensional stiffness $\quad \frac{E}{\rho g}$ [mm] $\qquad 8.0\times10^{9} \quad 6.3\times10^{9}$

2. Bending stiffness $\qquad \frac{\sqrt[2]{E}}{\rho g}\left[\frac{mm^2}{N^{\frac{1}{2}}}\right] \quad 2.3\times10^{4} \quad 2.6\times10^{4}$
   (Column buckling strength)

3. Plate buckling strength $\quad \frac{\sqrt[3]{E}}{\rho g}\left[\frac{mm^{\frac{7}{3}}}{N^{\frac{2}{3}}}\right] \quad 3.3\times10^{3} \quad 4.0\times10^{3}$

Fig. 24. Stiffness characteristics of composites which show the advantage offered by hollow fibres as reinforcing element (Ref. 38).

We succeeded in preparation of hollow carbon fibres (Fig.25) from wet spun hollow PAN-precursor fibres in a continously working laboratory equipment as miniplant. The carbon material of the hollow fibres has similar mechanical properties as that of type III C-fibres.

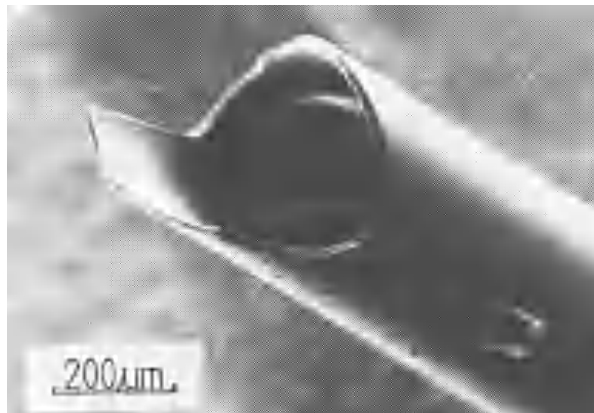But this development is only in a very early experimental stage.

Fig. 25. SEM of a C-hollow fibre from PAN precursor (Ref.37)

Finally, another form of composites should be referred, namely the combination of isotropic and anisotropic polymeric carbon in one combined all-carbon material, the carbon/carbon-composites. This material was developed in the past mainly for military reasons as conetip-and nozzle material in big missiles (Ref. 40).

However, carbon/carbon - composites offer such interesting combinations of properties that they will become of much more interest for many other applications. Results of basic studies on unidirectionally carbon fibre reinforced all-carbon composites (CFRC) can be found in the newer literature (Ref. 41 - 46). If isotropic matrix-carbon is used, up to 100 % utilization of the introduced fibre strength can be achieved by optimization of the complex liquid impregnation process.

If the carbon matrix itself is prepared with preferred orientation in direction parallel with the fibres (Fig. 26) it will contribute to the bulk modulus in the same amount as the fibre,and composites with stiffness of 400 GN/m^2 in fibre direction have been achieved (Ref. 47). Fig. 26 exhibits the sheet-like structure of the carbon matrix.
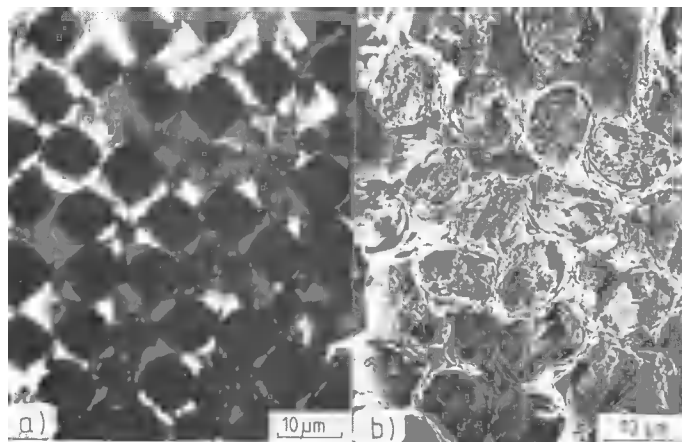
Fig. 26. Micrographs of unidirectionally reinforced carbon/
carbon composites with anisotropic carbon matrix, a) polarized
light after polishing, b) SEM after etching by oxidation in
air.

The achievable bulk data in strength and stiffness of carbon/carbon composi-
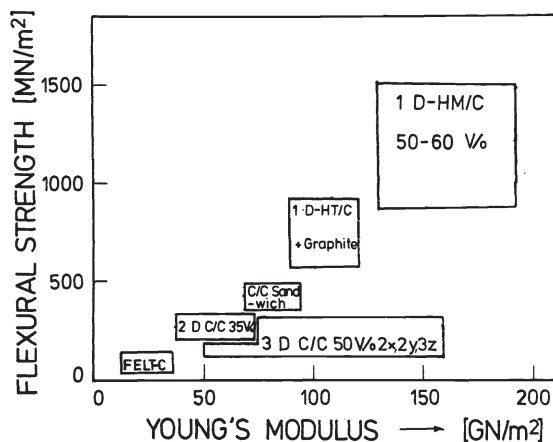tes with various arrangement of the reinforcing carbon fibres are compiled
in Fig. 27.

Fig. 27. Mechanical bulk properties of carbon/carbon compo-
sites [1,2,3-D indicates directions of reinforcement,
HM= type I, HT= type II, C/C sandwich was prepared by C-fibre
textiles (Ref. 46)] .

The variability in geometrical arrangement offers the possibility for tailo-
ring the properties of the composite. This f.i. is most important for medi-
cal application as implanation material. One of the most serious problems in
implantations surgery is that of the hip joints replacement.

The present solution for replacement of damaged hip joints with the steel
stem and a polyethylene soket is not finally satisfying. As known the avera-
ge life time of such an implantation is 5 years only.
An improvement is expected by the introduction of carbon materials, as shown
in Fig. 28. These developments are strongly supported by the German govern-
ment (Ref. 48). The friction and abrasion problem between ball and **socket**
seems to be soluble by the material combination of fine grained graphite
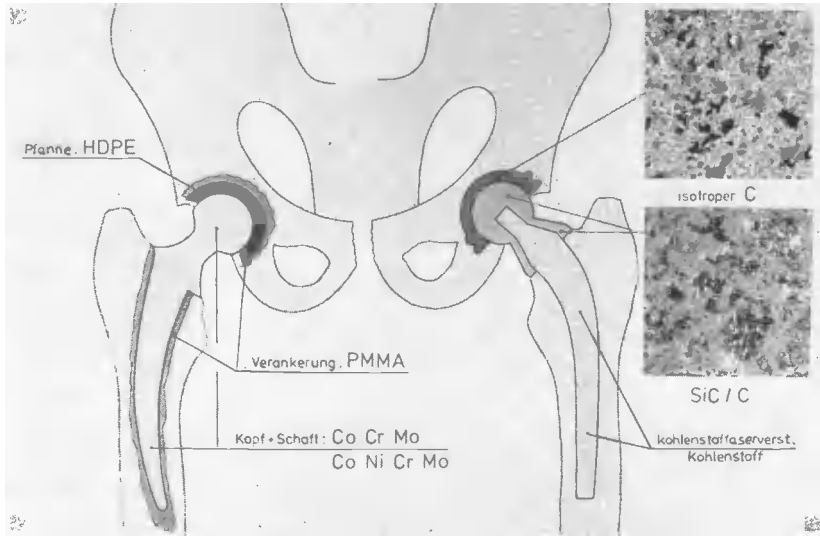with SiC impregnated graphite (Ref. 49).

Fig. 28. Material solutions for hip joint implantages left
side : present solution, right side: carbon solution (Ref.49).

The strength problem of the stem is hoped to be controlled by tailored car-
bon/carbon composites. One possibility of solution is indicated in Fig.29
(Ref. 24). It can also be recognized that intramedullary screw-thread is
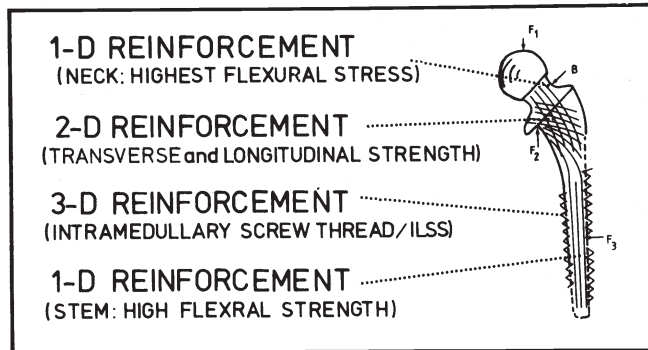foreseen for avoiding the unsatisfactory use of bone cement (Ref. 50).

Fig. 29. Possibilities offered by carbon/carbon composites
to imitate the femur structure for application as stem mate-
rial in hip joint implantations (Ref. 50).

It is hoped having shown that an enormeous field of application can be ex-
pected for polymeric carbon, in isotropic as well as in anisotropic form,
and in various combinations of both. Perhaps the reader will agree that the
way from polymers to polymeric carbon could be the key for a large variety
of future new materials. Polymeric carbon will not replace or substitute
the polymers, but it will improve these materials in a growing number of
applications.

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