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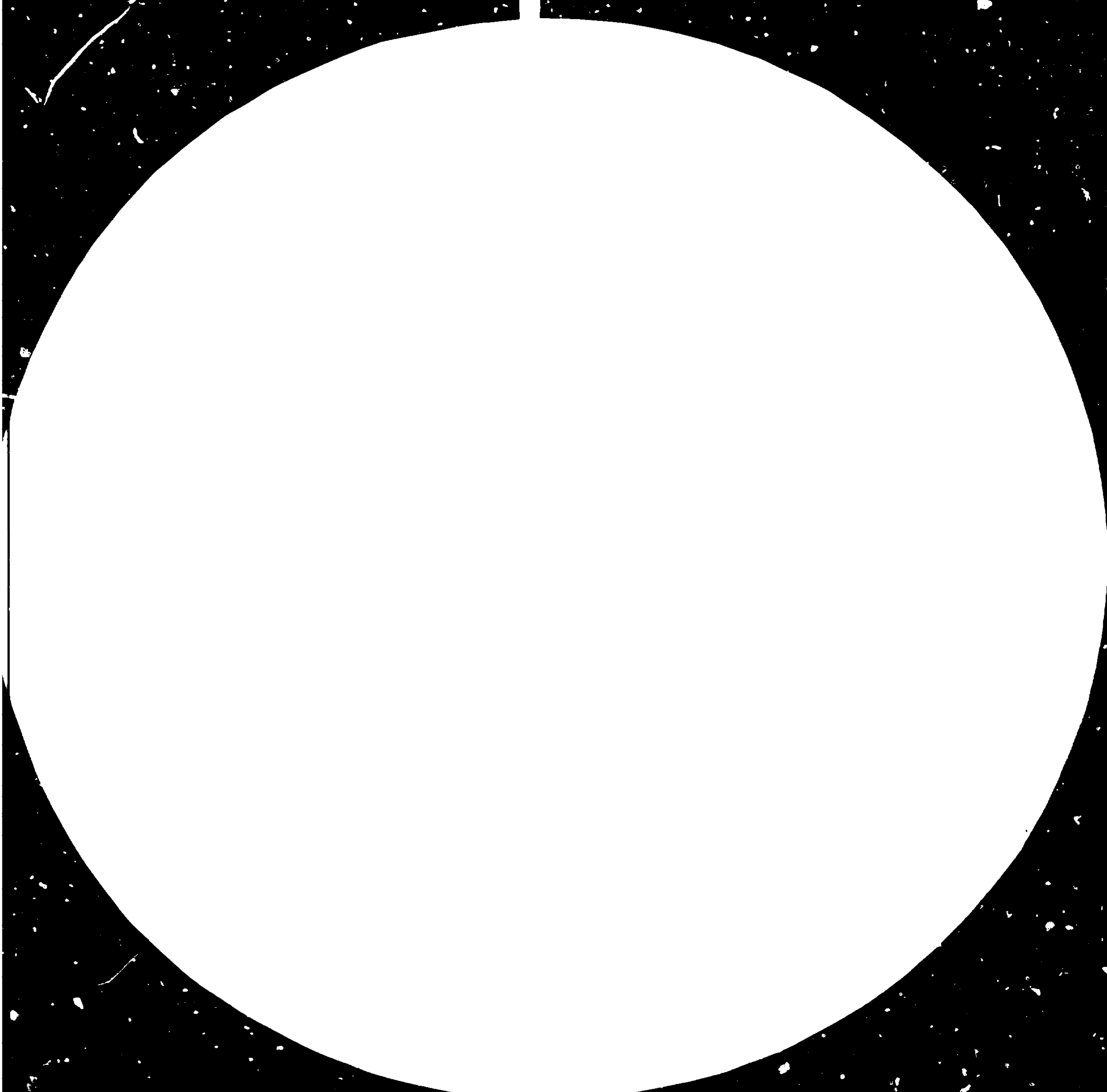

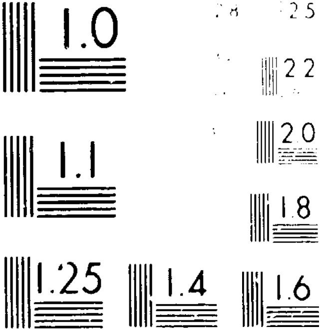

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FIBRE REINFORCED COMPOSITES*

by

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FIBRE REINFORCED COMPOSITES

Additionally two movies will be presented:

1. The automatic Celanese McLeanAnderson winding machine
2. Transportable bridge made from CFRP

Introduction

The reinforcement of polymers by glass fibres is known since 50 years. A successful technical application for high performance materials has started not before the late Fourthies because of lacking adhesion between fibre and matrix. This problem was solved only after World War II by bifunctional coupling agents. In case of unidirectional reinforcement with glass fibres the strength of the composite can be estimated by the rule of mixture. For instance with 50 v/% high quality glass fibres a strength of 1500 MN/m^2 can be expected in fibre direction.

The need for stiffness of such composite materials, as requested in the Fifthies by the aircraft and space industry, however, can never be fullfilled by glass fibre reinforcement.

The new generation of fibre reinforced polymers started with boron fibres of which the YOUNG's modulus exceeds that of the glass fibre considerably. Today, there remain only two types of reinforcing fibres with high stiffness - the polyaramid fibres and the carbon fibres. Because of the lower modulus and the limited applicability of the first one we will concentrate on carbon fibres only.

Besides of adequate fibre properties, adhesion and compatibility between fibre and matrix, the effect of fibre reinforcement of polymers is controlled by geometrical parameters, such as volume content and fibre arrangement. One must distinguish between endless fibres (fibre tows) and short fibres. The first ones should have lengths in the order of mm for carbon fibres for complete usage of the fibre strength capability. The advantage of continous fibres can be seen in the high volume fraction up to 60 % which can be introduced into polymer, the precise control of the fibre arrangement and the tailoring of pr ferred orientation of the composite. Short fibres have the tendency to random distribution in the matrix and their volume content is limited to at about 30 %. The main advantage of chopped fibres can be seen in the easy fabrication of composites and the possibility for subsequent reforming of them. Other forms of C-fibres such as textiles and felts are in their properties between both extreme cases the continuous and the short fibres.

The effect of reinforcement by high strength carbon fibres on composite strength is comparable with that of glass fibres. The YOUNG's modulus of the composite, however, is superior. For instance with 60 % fibres the values between 150 and 300 GN/m^2 can be achieved corresponding to 5 times the value of glass fibre reinforced composites.

These enormeous reinforcement effects are valid for unidirectionally reinforced composites parallel to the fibre direction, wher only a moderate increase in modulus and a strength somewhat belo matrix strength is measured in directions perpendicular to the fibre axis. In case of 2-dimensional reinforcement (angle-ply-technique) these differences in both directions are diminished. In case of isotropic reinforcement by short fibres the theoretical modulus and strength can be roughly estimated according to the equation

$$E_{Comp} = E_{Matrix} + \frac{1}{5} V_{Fibre} (E_{Fibre} - E_{Matrix})$$

E = YOUNG's modulus
V = Volume fraction

One disadvantage of C-fibre reinforced composites as compared with glass fibre reinforced ones is the limited strain-to-failure. Newest carbon fibre types show 1,9 % strain-to-failure compared with 4,4 % of the best glass fibres. Also for the matrix a lower limit for the strain-to-failure is requested. In general, one asks for 2 - 3 times higher elongation compared wi that of the fibre. This request however, is not yet fullfilled by today's high temperature resistant resins such as 180 °C curin epoxy resins with only 2 %, and polyimides with only 1,3 % maximum strain-to-failure.

Carbon fibre reinforced composites have been demonstrated as material of high performance during last year in an extremely spectacular manner by the successful flights and landings of the American space shuttle Columbia.

So far known, carbon fibre reinforced composites were used in the space shuttle for two most critical functional parts

1.) As carbon fibre reinforced polymer for the door of the loading room, which are opened during the flight in the orbit, but must be closed during take off and landing. Furthermore, the manipulator arm is nearly predestinated to be manufactured from CFRP.

2.) As carbon fibre reinforced carbons for the tip cone and the front wedges of the wings, parts which have a key position because they reach temperatures up to 1500 °C during entering the outer atmosphere.

Additionally carbon fibres were used as filler for the ductile cement for filling the slits between the 30 000 ceramic bricks on the surface of the shuttle.

This successful confirmation of the high performance of carbon fibre reinforced composites shown by the space shuttle flights offers a good basis for discussion of the preconditions which lead to such high quality composites.

First precondition is the reproducible quality of the carbon fibres and the availability of sufficiently large quantities of fibres to perform all tests on fibre properties. This includes a control of surface properties of the fibres and the influence of the adhesion between fibre and matrix. This question will be handled in the first chapter of this lecture.

Second precondition is the availability of high quality resins and the knowledge how to handle them for reproducible and strictly controlled fabrication process of the structural parts.For a successful application a third precondition is the exact precalculation of stress distribution in such anisotropic stuctural materials and subsequently the optimum design of such parts. Finally, a forth precondition is the availability of fabrication methods for CFRP. These last three preconditions will be discussed in chapter 2 of this paper.

In section 3 an introduction will be given into the technology of carbon/carbon composites as one of the most promising synthetic materials for the future and on the biomedical carbon materials for prosthetic devices.

1. Carbon fibres, their fabrication, properties and surface chemistry

The first technical application of carbon fibres started 100 years ago for EDISON's lamp. These fibres made from natural precursor (bamboo) were porous and had very poor mechanical properties. Nobody has expected, that chemically identical fibre materials will obtain the outstanding properties justifying even a revolution in material science. The newer carbon fibre technology started in the Sixties using rayon as precursor. Although these fibres were porous too, high mechanical quality with YOUNG's modulus up to 500 GN/m^2 and strength up to 2800 MN/m^2 were achieved by a hot working process at temperatures above 2800 °C. The very high price in the order of 1.000 US-Dollar/kg was caused by the difficult technology but became inhibitive for wider application of this material.

The period for more general technical application of carbon fibres started end of the Sixties with the use of polyacrylnitrile fibres as precursor. In this case, the preferred orientation of the polyaromatic carbon layers in fibre direction which is responsible for the outstanding mechancial properties is achieved by the much easier stretching process of the polymer precursor. Even these high quality carbon fibre got a competition during the Seventhies by the low price pitch based carbon fibres for which the preferred orientation is achieved during the melt spinning process. The mechanical properties of the resulting C-fibre, however, differ from those of the PAN based ones. The key for understanding of the properties of the various types of carbon fibres has to be seen in their microstructure.

1.1. The structure of carbon fibres

For such new materials as carbon fibres it is necessary to precise the characterization of structure. One can distinguish between :

1.) the crystalline structure
2.) the ultrastructure
3.) the microstructure , and
4.) the macrostructure

1.1.1. The crystalline structure describes the arrangement of the carbon atoms which is obtained by X-ray or electron diffraction. The basic structural concept remains the graphite lattice, however, with the restriction, that crystalline order in third direction is not present in general. The structural unit is the polyaromatic layer with strong σ -bonds between the carbon atoms (sp^2-hybridization). No indication of sp^3 - structural units have been found so far. Crosslinkage between polyaromatic layers, however, is precondition for high strength fibres.

From the theoretically calculated elastic constant C11 in a single crystal of graphite a YOUNG's modulus in a-direction of 1060 GN/m^2 can be derived. This value does not depend on the perfection of the graphite lattice in 3rd direction (c-direction). The C33 value indicating the YOUNG's modulus of 36.5 GN/m^2 in c-direction is more than one order of magnitude lower. The shear modulus C44 in direction parallel with the layer planes of 4.5 GN/m^2 is extremely low in an ideal graphite lattice. Therefore, perfect crystalline structure in c-direction has to be avoided for carbon fibres.

The structural units of carbon fibres as measured by X-ray diffraction are polyaromatic sheets with much less than 100 Å diameter. These data indicate only the areas of coherent diffraction, that means planar and defect free parts of the crystalline structure. A curvature of the graphitic planes f.i. appears as boundary of the sheet. Therefore the description of the crystalline structure is insufficient for a complete characterization of carbon fibres and for correlation of the structure with the fibre properties. TEM has corrected the previous picture of the ultrastructure based only on diffraction measurements.

1.1.2. The ultrastructure became effectively the key to explain the properties of carbon fibres. It describes the arrangement of carbon layers, each 100 Å broad, but indefinite in legnth. The first ultrastructural model for carbon fibres was presented by RULAND in the late Sixties. The two-dimensional model showing bundles of at about 20 parallel layers, was developed from measurements with stretch graphitized rayon based carbon fibres. At that time it was still an open question whether $\overline{11}$ direction or $\overline{10}$ direction is dominating the length of the layer. Now, it seems most probable, that $\overline{10}$ direction is parallel with the sheet length. That means, that the edges of the layer planes are formed by the leass reactive "chair" form. The RULAND model has been attacked strongly by later workers who have especially studied PAN based carbon fibres. The correlation between preferred orientation determined by X-ray and by mechanical measurement of the YOUNG's modulus, however, is confirmed even in newest publications. Latest model of ultrastructure was published 1981 basing on results of very sophisticated diffraction methods and combined with resulting chemical reactivity. The main item of this model is that the outer surface of a carbon fibre is not really formed from concentrically arranged polyaromatic layers but only by the bending back of folded layer packages. No edges of the layers are exposed to the surface. This causes low chemical reactivity of the fibre surface. In any case, this new model for ultrastructure of PAN based carbon fibres shows neither radial nor circular preferred orientation of the layer planes.

The radial arrangement has been really found in pitch based fibres. It was assumed that by perfect radial structure the sensibility of carbon fibres against shear and compressive streng can be diminished. Latest results of research in this field have shown, however, that the radial structure is a defect structure caused by splitting of the fibre during heat treatment. It is interesting to mention, that the micro- and the ultrastructure of pitch based carbon fibres is controlled by the liquid crystal like mesophase during spinning of the pitches and some kinds of disclinations can cause such internal stresses resulting in defects during heat treatment. These structural observations, however, fall under the term "microstructure" already.

1.1.3. Microstructure.

The term "microstructure" is mainly used for the results from optical and scanning electron microscopy. The scanning microscopy is very useful for carbon fibres especially if fracture surfaces are studied. These fracture surfaces give some indication on the ultrastructure,especially they explain radial and other orientations. It was tried to develop microstructure by eching of cross sections for instance by dry oxidation. Many microstructures are published, however, it seems that this technique is misleading.

As far as the optical microstructure is concerned, the preferred orientation can be recognized by areas of coherent light reflexion behaviour. Again, this technique is difficult to apply, because the resolution of optical microscopy is only 1/10 of the fibre diameters.

1.1.4. Macrostructure

The term "macrostructure" can be applied for description or appearance of the fibres such as endless or staple fibres, bundles, rovings, but also for the morphology of fibres cross sections. Round cross sections of the carbon fibres are obtained from wet spun PAN precursor, dog-bone like cross sections result from dry spun PAN precursor and wavely cross sections are found from rayon precursor. For useful application in composites round cross sections are preferred indicating , that wet spun PAN precursor is the most suitable raw material for high quality carbon fibres.

1.2. The properties of carbon fibres

Considering the mechanical properties of carbon fibres one has to start from theoretical values which can be expected from the knowledge of chemical bonding strength and preferred orientation in the fibres. In case of perfect polyaromatic carbon layers with complete preferred orientation in fibre direction the theoretical maximum value for YOUNG's modulus is 1060 GN/m^2. The maximum practically achieved YOUNG's moduli of carbon fibres are in the area of 70% of the theoretical value,however,with the disadvantage of high sensitivity against shear and compression stress. For practical purpose, therefore,one has to optimize the preffered orientation to preserve enough mechanical interlocking and chemical cross linking between the layer package and to avoid shear between the layers.

Also the strength of a carbon fibre can be precalculated theoretically if one exclude fracture initiation by notches. The theoretical strength corresponds to 1/10 of the YOUNG's modulus and is again expected to be dependent on the preferred orientation of the layer planes. Practically, one obtains maximum strength values of about 1 % of the theoretically expected value because of the many flaws and surface defects acting as notches.

Heat treatment of carbon fibres in the temperature range between 1300 and 2800 °C has a strong influence on the crystalline and the ultra structure. The defects within the layers decrease and the parallel orientation of the layers increases, but the cross linking between the layers decreases.

Therefore, the application of highest final heattreatment temperatures increases the YOUNG's modulus but decreases the strength of the carbon fibre. PAN based fibres heat treated at 1350 °C exhibit in best cases a strength of 4500 MN/m^2 and a YOUNG's modulus of about 240 GN/m^2. These carbon fibres heat treated up to 2800 °C reach YOUNG's modulus values up to 450 GN/m^2, the strength,however,decreases below 3000 MN/m^2. The pitch based carbon fibres are even more sensitive against the effect and enhanced increase of preferred orientation. The YOUNG's modulus shifts from 350 to 550 GN/m^2, the strength,however, does not exceed 2000 MN/m^2.

The prices for the various carbon fibre types vary strongly depending on raw material and final heat treatment. In general it is claimed that pitch based carbon fibres are lower in price than PAN based carbon fibres, however, the difference in price seems to be neglectable. PAN based high strength carbon fibres (so-called HT-types) are offered today with 50 Dollar/kg, and pitch based carbon fibres with lowest final heat treatment (P 55), which YOUNG's modulus is higher but strength is lower than that of the HT-type, cost the same.

High modulus fibres, these are the high temperature treated carbon fibres cost 300 Dollar/kg if PAN based (so-called HM-types). Pitch based high module fibres range between the above mentioned 50 and 1000 US-Dollar/kg depending on the level of YOUNG's modulus. S-glass fibres cost less than 10 Dollar/kg, polyaramid fibres at about 25 Dollar/kg. Basing on these data, one can compare the costs of equivalent amount of strength and modulus for glass, polyaramid, PAN and pitch based C-fibres.

It will be discussed in the following chapter that there is a possibility to reduce furtherly the costs of PAN based fibres if a multitow textile PAN precursor is used.

As far as strain-to-failure is concerned, carbon fibres show brittle fracture behaviour in any case, that means the strain is controlled by elastic deformation exclusively. In case of high strength PAN based carbon fibres newest qualities show a strain-to-failure of 1,9%. Further increase can be expected only if further increase of strength is possible. The high modulus fibres, especially the pitch based ones with modulus of 50/GN/m^2 and more, but strength in the range of 2000 MN/m^2 have a strain-to-failure of 0,4 % only.

The disadvantage of low strain-to-failure of the high stiff carbon fibres can partly be compensated in hybride composites by addition of high strength glass fibres or polyaramide fibres.

1.3. Today's fabrication of carbon fibres and tendencies in future

As nearly all carbon fibre reinforced composites used for high performance application are based on PAN fibre precursor, this fabrication process will be discussed mainly.

1.3.1. Carbon fibres from PAN

The fabrication of carbon fibres from PAN consists of two main steps. In the first one, the polymer fibre consisting of polyacrylnitrile in form of polymer chains is cyclized to a heteroaromatic ladder polymer with nitrogen still remaining in the aromatic rings. During the second process step, the therma degradation treatment, the C/N-bonds in the heteroaromatic ladders are ruptured, the nitrogen content is volatilzed and planar carbon sheets are formed. The most difficult process step is that of stabilization treatment because of the exothermic reactions which must be performed very slowly to avoid overheating and it takes hours. This cyclization reaction is strongly influenced by the chemical composition of the polymer fibre as well as by the stabilization atmosphere temperature and residence time. There exist patents describing stabilization catalysts which can be copolymerized with acrylonitrile such as methylacrylate, acrylic acid, itaconic acid, allyle alcohol and others. The effect of such copolymers should not be seen only in the shortening of stabilization time, but also in an increase of mechanical properties of the resulting carbon fibres. This has been found by us for itaconic acid, which diminishes the volatile byproducts and increases the stabilization rate, but also the final fibre properties. Methylacrylate is mostly used as copolymer in textile PAN fibres because of widening of the softening temperature range, and therefore because of easier textile stretching treatment for PAN fibres. It was found that from the viewpoint of mechanical properties of carbon fibres a low content of at about 2 % only is favourable.

Stabilization treatment is performed mainly in air indicating that a dehydrogenation reaction occurs during this process step in addition to the thermally activated cyclization. Oxygen reduces the cyclization rate however, but some copolymers such as itaconic ccid compensate this undesired byeffect of oxygen.

The final mechanical properties of the carbon fibre are strongly influenced by the molecular structure of the polymer. YOUNG's modulus and strength of the carbon fibre are effectively a mirror of the corresponding data of the PAN precursor fibre. This correlation shows that the arrangement of the chain molecules in the precursor fibre is of decisive influence on the arrangement of the carbon sheets formed in the final carbon fibre. As a consequence the prestretching treatment of the polymer fibre before stabilization influences strongly the resulting stabilization reactions and the final carbon fibre properties. In any case, the stabilization has to be performed under conditions which hinder shrinkage of the fibre.

There exists only a limited number of chemical companies which produce PAN fibres for the world market. Different PAN spinning processes are used, dry spinning on one hand and wet spinning processes with various coagulation bathes on the other. It has been mentioned before, the wet spinning is more suitable because of the circular cross section of the resulting carbon fibres. It seems that organic coagulation bathes are more suitable than inorganic ones because no mineralic residues remain in the PAN fibre. Such mineralic residues can damage the carbon fibres during carbonization and after treatment. Also clean spinning conditions are very important as has been shown by British workers. The tensile strength dependence on the gauge length during the tensile test indicates defects and notches mainly if spinning was not performed under very clean room conditions. Similar strength reducing effects are caused by rough polymer surfaces. Modern precursor factories use improved spinning processes to guarant very smooth PAN fibre surfaces.

1.3.2. Pitch based carbon fibres.

Carbon fibres made from petrole-pitch are known since many years, however, the mechanical properties of such carbon fibres are very poor, and the material is only used for thermal insulation purposes or as filler material for several polymer matrices. There exists a possibility to improve the mechanical properties of such carbon fibres from pitch by the difficult hot stretching process at graphitization temperatures as has been applied before the rayon based carbon fibres.

A realistic manufacture process for high quality carbon fibres from pitch was introduced by one American carbon company using the so-called mesophase pitch as raw material. Pitches consist of many thousands of different aromatic molecules and have the tendency to form larger planar polyaromatics during heat treatment which themselves can form liquid crystal like mesophases. Such a mesophase show the same behaviour as nematic liquid crystals. Under the influence of surface tension small spherical particles coalesce to larger ones until all isotropic pitch matrix is consumed by this structures with preferred orientation. Such mesophase containing pitch can be melt spun. The resulting pitch fibre can be stretched at elevated temperatures. Before cooling it must be stabilized by oxidation to avoid further melting during carbonization heat treatment. There does not exist enough scientific literature on this process. The experience has shown , that the simultaneous melt spinning of thousands of monofilaments introduces many difficulties during production. In principle, the process can be compared with the dry spinning process of PAN which differs decisively from the more economic wet spinning process because of similar reasons.

The original raw material petroleum-pitch is considerably less expensive than the polymer material fror PAN fibre spinning. The pitch to be used for the above described spinning process however has to be pre-treated, that means purified from unsoluble components and heat treated to form a mesophase or to preform mesophase pitches. It does not exist any information about the costs of this purification and pretreatment process.

The carbon yield of pitch fibres after carbonization with 80 to 90 % is superior as compared with the carbon yield of stabilized PAN between 50 and 60 %. The main advantage of pitch based carbon fibres is the high YOUNG's modulus and especially the possibility to increase easily YOUNG's modulus by heat treatment. The disadvantage are their much lower strength and the much broader strength distribution as compared with those of PAN based carbon fibres. The final situation in commercial availability of high performance pitch based carbon fibres is not yet to estimate.

1.3.3. World capacity in fibre production and future tendencies

The world capacity for carbon fibres is estimated with 2000 to/year in 1981. This capacity is installed with at about 1/3 in international chemical industries, 1/3 in carbon and graphite industries and 1/3 in textile industry and companies manufacturing serie products Most of these industries will strongly expand their capacity during 1982 and the following years. It seems that PAN will remain the dominant raw material for high quality carbon fibres in any case. As will be discussed in chapter "application" later on , the today's production is used for military purposes, civil aircrafts, aerospace technology and sporting goods. More general application in machinery and other fields is of minor importance at this time. For application in automotive industry and others which would promise a very extended market, the prices of the carbon fibres must decrease even more drastically.

One way to reach this goal is the application of heavy tow textile PAN precursor which is available on the world market at costs below 2 US-Dollar/kg. That means with 50 % carbon yield the carbon fibre raw material will cost below 4 Dollar/kg. Under these preconditions, the reduction of raw material costs by use of pitch can be neglected. However, the spinning costs of PAN multi tows with 160 or 320 thousands of monofilaments is technically realized and inexpensive, whereas melt spinning of limited number of monofilaments simultaneously, I would estimate 2000 as maximum, should cause much higher production costs, thus compensating the cost reduction of raw material. It was shown during last year, that the quality of carbon fibres from commercial available heavy tows increases progressively and reaches already 80 % of the quality of the carbon fibres made from special PAN precursor with 3000 monofilaments. The cost projection for carbon fibres in heavy tow form during next years shows final prices between 20 and 30 Dollar/kg. It can be imagined hardly that pitch fibres will beat this level.

1.4. Surface properties of carbon fibres.

As mentioned in the introduction the final properties of a composite are controlled by the mechanical properties of the fibre and the matrix and by the interaction between fibre and matrix. In case of glass fibre reinforced polymers it has taken more than 20 years to solve this adhesion problem for technical application. Although the adhesion problem is less severe in the case of carbon fibre reinforced polymers it must be taken into consideration, because graphite like planar surface layers have a low chemical reactivity in general.

A good adhesion is absolutely necessary to guarant stress transfer from matrix to fibre under tension, compression and shear. The interlaminar shear test is the routine method to give quantitative information on the transfer of stress from fibre to matrix. A more realistic method for characterizing the adhesion is the tensile-tortional test of circumferentially wound tubes measuring the transverse strength at different tortional angles. Angle 0 means transverse tensile strength, Angle 90 means pure shear strength.

Commercially available carbon fibres have a so-called sizing - in most cases an epoxy resin without hardener. This coating serves primaryly as protection of the yarn during handling. It can also act as coupling agent, however. The exact mechanism of adhesion between the fibre surface and the sizing or the matrix polymer is not yet completely cleared. There are three possibilities: only mechanical interlocking, a physical adhesion or a chemical coupling.

It has been proved and recently confirmed by us that chemical coupling is a dominatin parameter. The chemical coupling is based on the surface oxides on carbon fibres which can react with functional groups of the matrix. Surface oxides can be of acidic or basic nature. Consequently, amino groups, hydroxyl-groups, epoxy groups and other functional groups of the resin are able to form stable covalent chemical bonds.

Such surface oxides are always present on carbon surfaces, in high amount on disordered carbons, in less amount on graphitized carbons. Controlled formation of such oxides in higher surface concentration can be achieved by wet oxidation treatment such as in nitric acid or others, by anodic oxidation or by dry oxidation at elevated temperatures in oxidizing atmosphere. It is known which methods are applied by industrial producers for the commercial so-called surface treated carbon fibres. In case of high strength fibres (maximum heat treatment temperature in the 1400 °C range) thermal treatment in air is obviously sufficient to obtain a translation of fibre strength into the composite up to 90 %. The surface treatment problem is more severe for high modulus fibres because of their very smooth surface and is most critical for pitch based high modulus fibres. It has been found by us, however, that for instance wet oxidation in salpetric acid can improve the translation of fibre strength from 50% with non treated fibres up to nearly 100 % after oxidation treatment. These studies were performed with phenolic as well as epoxy matrix, both polymers with functional groups.

In case of a polymer without functional groups like polyolefins surface oxides can not react with the matrix,and the translation of fibre strength and modulus is very poor (30% only) For polypropylene it has been found that this problem can be solved by grafting of the polymer with for instance acrylic acid. Under these conditions and using bifunctional amines as coupling and curing agent translations of fibre strength up to 60 % were achieved in the composite with thermoplastic matrix.

2. Polymeric matrix materials, fabrication methods for composites and to-days application

2.1. State of polymeric matrix materials and tendencies for further developments

The main matrix materials for fibre reinforced polymers are thermosetting resins. In the beginning of application of glass fibres reinforced composites phenolics were the only used resins. Because of their disadvantage of water formation during curing and the need of high curing pressures, today mostly polyesters are used as matrix for glass fibre reinforcement. It can not be excluded, however, that phenolics will come back again because they have very high chemical and thermal resistance. Fibre reinforced furane resins are already used as corrosion resistant new material in chemical industry.

For graphite fibres epoxy resins are superior as compared with polyesters, mainly because of their superior mecanical and thermal properties, especially better resistance against fatigue. Furthermore, it is known that composites of large dimensions under very high load show intrinsic heating if polyester is used. In case of glass fibre such extreme loads are never applied The disadvantage of epoxy resins is not only their higher price but also the longer residence time needed for curing. For pulltrusion f.i. it is difficult to apply epoxy matrix.

Epoxy systems need a prepolymer with epoxy groups and a hardener. For application in composites one has to apply a "one component system". The standard components for high quality epoxy resins are bisphenol A-diglycidyl ether (DGEBA), and a multifunctional hardener for instance 4.4' diaminodiphenylmethan. New developments are hydrogenated bisphenol A-diglycidylether and the bisphenol F. These systems have a better stability against water and nvironmental attack, what is most important for application where changes in temperature, humidity and pressure occur rapidly e.g. in aircraft, aerospace or in space shuttle systems.

Multifunctional epoxy resins show an even better cross linkage and therefore a higher mechanical and thermal stability, e.g. tetraglycidylether of methylenedianiline (TGMDA) or triglycidylether of p-aminophenole (GTPAP). All commercial epoxy systems are blended, mostly with DGEBA for control of the viscosity. One tries also to shorten the curing cycles which range between half and some hours today. For this purpose the use of cationic polymerization initiators like diphenyljodonium salts or triphenylsulfonium salts would be a possible solution. They act as catalyst and are used in combination with copper salts as accelerator. Curing can be achieved in the range of minutes at 120 as well as at 180 °C. A typical commercial product of this type has been the socalled ARNOX 3110 of General Electric for which curing time of 3 minutes at 140 °C were claimed. Unfortunately, this product was withdrawn from the market just recently because of toxic reasons.

It was mentioned that epoxy systems are nearly exclusively used today as matrix materials because of their superior mechanical properties. For general technical application so called 120°C resin systems are established, for aircraft application 180 °C (resins temperatures defining curing temperatures). These resins have a maximum application temperature of 80 °C and 140 °C respectively, which can be applied without significant loss of mechanical properties. The successfull increase of the temperature resistivity is combined with the disadvantage of increased embrittlement and reduced strain-to-failure down below 2 %. An enhanced development in this direction is the use of polyimidies as matrix material with higher thermostabilities up to 250 °C but strain-to-failure in the range of and even below 1 %.

Developments in the contrary direction are concerned with the increase of the formability of composites if the disadvantage of poorer mechanical properties and lower temperature stability can be tolerated. The most important step in this direction is the application of so-called vinylester resins (acrylates based on bisphenol A. Such materials are used for sheet molding compounds("SMC-techniques").

Finally, a not yet solved problem in application of epoxy resins must be mentioned. That is the limited shelf life of prepregs. Such component systems will loose resin flow and tack within about 6 months even during refrigerated storage. Less reactivity of the resin would be desirable from the viewpoint of storage lifetime with the disadvantage of slower curing. Nearly all commercially applied prepregs consist of epoxy mixtures containing TGMDA. It appears possible that also polyester resins with isophatic acid as main component will gain importance as matrix for CFRP in future.

Now-a-days, the reinforcement of thermoplastics is coming. Already in practical application are carbon fibre reinforced polyamides. Especially in the United States these materials are used for injection molding and other fabrication processes. Up to 25 v/% carbon fibres are used in these materials. It is expected that application of C-fibre reinforced polyamides will expand widely in the near future. Polysulfons have been described in some application in aircraft structural elements already. Finally, polyolefines can be reinforced by carbon fibres as we have seen before, when reactive groups into the polyolefine are introduced by grafting.

With the cost of carbon fibres in the past, the cost for the matrix as well as for processing was neglected. In future, however, one has to consider this matrix costs in relation with the expected fibre costs. Under the assumption of 50 v/% heavy tow PAN based carbon fibres the matrix costs will be 10 % in case of polypropylene, 3o - 50 % in case of epoxy and more than 100 % in case of polyimides.

2.2. Fabrication techniques for the economic production of carbon fibre reinforced composites

2.2.1. Wetwinding

The wetwinding technique for fabrication of fibre reinforced polymers as applied today is proved since years as very suitable for the preparation of prototypes and for small scale production of composites. It is too time consuming for mass-production.

Filament winding is successfully applied for the fabrication of pressure vessels in aerospace application or for tubular structural elements in various fields of applications. Very big structures have been produced in this way as protoptyes. Structural elements comprising the whole body element of large airplanes or submarines are principally producable by this technique. Wet winding technique, however, is not yet suitable for economic large scale fabrication of modern composite materials.

In conventional filament winders the rovings of the filaments have to move along the axis of the structural element. The exact angles of the fibre layers are of greatest importance. Some progress was achieved by the use of micro computer controlled multi axis winders. In this way, even most sophisticated patterns can be fabricated with high performance.

Another solution to improve the wet winding technique for fast production is the GOLDWORTHY Engineering development. Ring-sahped winding system traverses and orbits a stationary mandrel in ringwinder unit , designed for high-speed production of complex parts. (Photo, Goldsworthy Engineering)

The newest development is the fabular CELANESE McLean Andersen winding machinery. The principle is that all fibres are drawn through a resin bath by moving the axis of the structural elements as mandrel for the wet winding component in front of the fibres.

Further process steps have to follow the wet winding step such as bandaging, pressing, drying, curing and remove of the mandrel.

In some modern industrial pilot fabrications these subsequent steps became rate controlling for the overall process and not more the winding step itself because of its improved speed.

2.2.2. Pultrusion

An alternative for mass production of tubes and profiles of infinite length would be the pultrusion. The problem with application of this technique for fabrication of carbon fibre composites has to be seen in the long curing time of epoxy. In contrary, polyester with very short curing times can be easily applied for pultrusion. It is hoped that with the new types of epoxy and especially hardener systems pultrusion techniques can be introduced successfully for economic production of carbon fibre reinforced epoxy material.

2.2.3. Prepreg technique

Classic fabrication technique for carbon fibre reinforced high quality and high performance composite materials is the application of prepregs,

By a lay-up technique one can manufacture very precisely composites with a fibre orientation as precalculated in advanced design. All parts in aircraft and other critical applications are manufactured by this prepreg techniques.

A new technique was developped for fabrication of prepregs with short fibres in which nearly complete preferred orientation is achieved. Such prepregs have the advantage to be used in same way for the lay-up technique as usual prepregs with endless fibres but additionally the composites can be molded partly to more complex shapes before curing. Structural elements with sinus curvature were successfully fabricated in this way .

2.2.4. Sheet molding technique

Finally, the sheet molding technique seems to be a most promising technique. This is a compromise between lay-up technique and injection molding, that means one can make prepreg layers of thickness up to 5 to 6 mm with a high formability. Such prepregs look like made from leather. This material can be molded in prepared molds by pressure more easily.

2.2.5. Injection molding

Thermoplastic polymers filled with short fibres can be processed by injection molding in known manner. Also by this technique some preferred orientation of the fibres is obtained automatically, though not always wanted. For a better control of this effect Intensive development work is performed especially in the Center of Composite Materials at the University of Delaware.

2.3. Application of carbon fibre reinforced polymers

The properties of composites are superior in strength, fatigue and corrosion, as compared with steel and aluminium. The costs are at the moment still incomparable with those made from routine materials. These costs are mainly controlled by the high costs of carbon fibre materials. Therefore, today's application is limited to aerospace and aircraft industry where the weigth advantage is decisive in spite of the costs of the materials. Furthermore, advanced sporting goods are preferably made from carbon fibres because in such cases the endprice tolerates high carbon fibre costs. Also in medical application costs can be neglected. The critical cost question arrives for mass application in mechanical industries such as in transportation and automotives. Only if the cost problem is solved a brodaer application can be expected as estimated for the end of the 20th century.

2.3.1. Application in aerospace industry

The successful application of CFRP in the space shuttle was mentioned in the introduction. One has to ask, why only the doors were made from this material and not also other parts. The answer is given by the NASA doctrine at that time of drastic shrinkage of the budget available for this experiment, namely : "Low cost - Low risk !" The cost limits were discussed already. The level of the risk-limits depends on the availability of conventional materials as alternatives. In case of the manned space shuttle of the NASA the material solution with lowest risk was aluminium for the whole structure. Only the resulting overweight has forced the designer to use the composite-alternative for the structural parts with highest weight gain in spite of the high risk because of first application in a primary structure of a manned flight vehicle. From the same reason aluminium was used for the first version of the manipulator arm, although the composite version is already available. In non-manned flight vehicles for the space the risk level is much lower and CFRP's are widely used for various parts such as missile structures, solar mirrors, antennas and others.

One example is the tip cone of the Aries missile developed for civil application in Germany and designed in CFRP with a wall thickness of 4 mm only and a total weigth of 40 kg. In this case the weight saving is 70 % if compared with a design in aluminium. Widely used are fibre reinforced polymers for fuel tanks in missiles, both polyaramide in C-fibres are applied for this purpose.

2.3.2. Application in military and commercial aircrafts

As mentioned before, military aircrafts can be seen as pioneers in application of carbon fibre reinforced composites. First applications were restricted to so-called ternary and later secondary structural elements. Mainly parts of the body, the vertical stabilizer, the horizontal stabilizer and the ruder assembly, and especially the leading etches in stabilizer and wings are made from C-fibre reinforced composites.

Only as recent developments also primary structures are applied in such aircrafts, e.g. engine duct in F 100. Most interesting is a proposed aircraft structure containing more than 60 % of all materials in carbon fibre reinforced polymers.

The achieved weight saving is calculated for the different parts and range between 20 and 40 %.

Before applied in such aircrafts very careful tests have been performed. Especially all tests on aircrafts parts in laboraotry must be fitted to the practical loading conditions.

For commercial airplanes the tests are even more critical. Various small structural parts were selected for years long tests by various airlines in cargo flights with a total of flight experience up to 2 millions hours and more.

Today, the new commercial aircrafts Boeing types 767 and 757, as well as the airbus A 310 are representative for application of CFRP parts. As most advanced commercial airplane the Lear Fan 2100 must be referred which whole structure is made from CFRP, however, the licence is not yet inparted by the aeronautic authorities.

Also in heliocopters C-fibre reinforced composites are applied not only for the rotor blades but also for the structure.

Most profit from the high stiffness of C-fibre composites are drawn for the gliders. The world champion glider consists of carbon fibre reinforced beams for the extremely long wings and for the body. Newest developments are telescope like wings made from these C-fibre reinforced composites.

2.3.3. Application of CFRPs in sporting goods

Contrary to the application of C-fibre reinforced composites in aerospace and in aircrafts, the application in sporting goods was practically without any risks. Also the limitation of low costs were neglectable. The main reason for application was the weigth saving and the improvement in stiffness. Application was started for sailing mast in champion ships, as structure of racing boats and also as bicycle frame.
A wider application started with skis, tennis rackets, fishing rods and most of all with golf shafts. The application of carbon fibres for golf shafts was the largest one for non-military purposes since years. In all statistics application for sporting goods appears at about 50 % of the total carbon fibre consumption. This success in traditional equipments was achieved in competition with the highly developed conventional materials such as multi layer of wood in skis and tennis rackets. In future equipment of new sport disciplines carbon fibre reinforced polymers will be used from the beginning, for instance in boards for wind surfing

2.3.4. C-fibre reinforced composites in automotive industry

One of the most interesting fields of application for all new materials is the automotive industry because of the very high volume, especially for the mass production of one special type. Under the precondition that the technical properties of a new material are suitable, the cost limits are extremely low in this industry. This is valid not only for the material cost itself but also for the cost of fabrication of the single parts as well as for their assembling.

Besides of this intrinsic driving force of the automotive industry to apply CFRPs , the additional Governmental influence within the energy saving programmes was most important. The FORD company as a pioneer has demonstrated that drastic weight saving can be achieved if as many as possible of metallic parts are substituted by composites without modification of the overall design of the traditional big American limousines.

Potential automotive application for advanced composites are

a) in the drivertrain as driveshafts, wheels, brakes, real axle housing, gears, real axle, transmission housing;

b) for chassis and suspension such as leaf and coil springs, frames torsion bars, upper and lower arms;

c) for the engine: connecting rods, push rods, pump housing, cover plates, intake manifolds, cylinder block, fly wheels , and finally

d) for the body sheet and structure: panels, pillars, stressed skin design.

Although this demonstration was successfull in principle, there remains further need for development for mass application: firstly, because the design of the various parts and also the whole design of such a composed structure must be changed to utilize the specific properties of these new anisotropic but tailorable materials, and secondly, the fabrication methods must be improved for mass production. It was reported, that this demonstration car has caused enormeous total costs up to 3 million dollars for development and fabrication. Cost reduction can be expected if mass production will start. In aircrafts industry with small production numbers the cost reduction if production follows the prototype is about 75%. In automotive industry the cost reduction between prototype and mass production is 98 %.

Weight reduction in the automotive industry will save fuel consumption. In case substituting steel up to 50 %, in case of substituting aluminium 40 %. For the United States of America, a total gasoline saving of 7 billions gallons is forecasted for 1990.

From today's viewpont a replacement of steel by C-fibre reinforced composites is most promising for springs and for the drive shaft. Besides of the weigth saving, CFRPs solve successfully the vibration problem. For a critical rotation number of 7200 cycles per minute for instance, shafts with a total length of 2,5 m can be applied without splitting into two parts, what is needed for driveshafts made from steel. CFRP driveshafts are multi layer composites with angle ply arrangement and different winding patterns. The American development is based on the use of pure carbon fibres, the European one uses high modulus carbon fibres in combination with 80 % of glass fibres as hybride. The hybride version had a little lower fatigue strength as the pure carbon version (after 1 million cycles fatigue strength of 40 MN/m^2 is measured against 60 MN/m^2 with pure carbon fibres).

In the beginning the connection problems between CFRP and metallic parts were critical for the application. These problems are solved today satisfactoring. Pilot production of driveshafts is started in Europe and in technical tests with all automotive companies.

Besides of the driveshafts, leave springs made from CFRP are already in technical application for trucks. Also sections of the frame are made from this material.

2.3.5. Other technical applications of carbon fibre reinforced composites

A review on application possibilities must remain incomplete because effective applications were limited by the former high costs of carbon fibres. Nevertheless, such a preliminary general review can initiate some imagination, what further application may be expected.

2.3.5.1. Application in wind channels, wind mills and air compressors

C-fibre reinforced rotor blades are used in the supersonic European wind channel with blades length of at about 2,5 m. Another application are the rotors in modern wind energy convertors, again in a European experiment with total length of the rotors of at about 50 m.

Similar application is that of CFRPs for compression blades in gas turbines. This application reminds on the successless introduction of this material by Rolls Royce years ago. The new and improved materials,however, may successfully be used in gas turbines for non aircrafts application.

'.3.5.2. CFRP in transportation

The very light CFRPs seem to be ideal materials for application in transportation ,such as containers,railways and others. A prototype already applied is the single rail Japanese super train. Reduced costs of the carbon fibres will open this field of application in future.

2.3.5.3. CFRP in machineries

In machine industries CFRP will be applied preferentially for high speed parts. A successfull application is described for gliding blocks in waving equipments. But also for housings of analytical equipments C-fibre reinforced polymers are used already because of their antistatic properties.

Finally, the low absorption of carbon and polymers for X-ray radiation has opened the application as X-ray caskets but also as X-ray tables in medical application. Also surgery tools are made from CFRPs if X-ray observation is used simultaneously.

2.3.5.4. CFRP in acustic application

It is very interesting that the high stiffness of CFRPs can be used for all parts where acustic properties are required, such as in loud-speakers. Especially in Japanese production the C-fibre reinforced loud-speakers are standard products already.

More exotic is the application in music instruments like in guitars. It has been also shown in a very interesting experiment by Canadian workers that violins with the same dimensions as the original Stradivari violins and made of CFRPs have not only comparable but even superior resonance properties.

2.3.5.5. Application in civil engineering

It will be still a long way to introduce CFRP in civil engineering as replacement of ceramic materials or even of wood. Most chances are for the case where such composites can replace metallic structures. For bridges for instance, it is known that more than 80 % of the materials of the beams are used for supporting the own weight of the beam only.

It was proved recently, that main load carring parts in transportable bridges can be made from CFRPs. Although this experiment was a military one, it is hoped that also for civil application , especially in development countries, such portable bridges will be introduced in future.

3. Carbon fibre reinforced composites with carbon matrix and biomedical application of C-fibre materials

Carbon fibre reinforced polymers have one main disadvantage, that is the same as with all polymers: their instability at elevated temperatures The high thermal stability of the carbon fibre itself which ranges up to temperatures of 2000 °C is thus not really used. This disadvantage is eliminated if carbon itself is used as matrix in carbon fibre reinforced composites. The trivial name for this material is carbon/carbon composite.

Besides of the high temperature resistance of such carbon composite materials, also the extremely good biocompatibility of carbon can be used.

3.1. Carbon/Carbon Composites

It has been shown in the introduction, that carbon/carbon composites are applied successfully in the space shuttle. They can be seen as a key material for these severe requirements during re-entering in the air atmosphere because of the very high stagnation temperatures at the nose tip and the wing etches of the shuttle. Carbon/carbon composites can be seen as one of the most exiting materials developed during the last decades. It is hoped that they will be applied also in other parts of engineering.

Carbon/carbon composites are mainly 3-dimensionally reinforced materials. Thus, they can be seen as quasi isotropic. The fabrication consists of wet winding, carbonization of the matrix and multiple reimpregnation and recarbonization steps. The first carbonization of the resin results in a very weak composite in which the 3-dimensionally arranged fibres are only fixed in their position without any technological value of the composites. Such carbon/carbon skeleton is then impregnated mainly by pitch and recarbonized up to 6 times. Finally, one ends in bulk densities of at about 1.9, and in laboratory experiments even of 2.00. The theoretical density of a perfect graphite lattice is 2.26.

As mentioned in the introduction the special application of carbon/carbon composites in the space shuttle required oxidation resistant coatings which were made by impregnation with silicon carbide, using pack cementation treatment. It is the advantage of the NASA work on carbon/carbon composites, that all fabrication details are published.

We have performed similar coating experiments with polygranular carbon and graphite by pack cementation or vapour deposition. Very often, the silicon carbide layer exposes slits and pores, and does not provide a perfect protection against oxidation. The solution in the space shuttle application was additional impregnation with silica ester and thus formation of a silicon oxide filling up the pores.

Also test results before application in space were published by NASA, and it was shown that this silicate impregnation **reduces** the mass loss under oxygen and reduced pressure at 1000 ^{o}C considerably. This is a simulation of the environment conditions during entering into the atmosphere.

3-dimensional reinforced carbon/carbon composites can be made by various techniques. French Aerospaciale Company has developed already a waving system where 3-dimensional textiles can be fabricated automatically. SEP, a French corporation has another process by means of which also multidirectionally that means more than 3-dimensionally reinforced materials can be prepared by combination of carbon fibre carbon prepregs in form of thin rods which are combined to the various structures and than densified by repeated impregnation and recarbonization.
In 3-dimensional composites fracture does not exhibit the behaviour of a classic brittle fracture. As advantage of such 3- dimensional composites fracture propagation is stopped or hindered by the fibres in the various directions and by the pores between matrix and fibre bundles.

The effect of such micro porosity within the carbon/carbon composites is a pseudo ductile fracture behaviour. No catastrophic fracture of the composite is observed.

At very high testing temperatures of 3000 °C the carbon/carbon composites behave completely different. The slits between the structural elements are closed because of thermal expansion, but always a ductile fracture behaviour is found.

C/C composites have been found application as parts for missiles for example in solid fuel engines. Nozzles are used of 3-dimensionally C/C composites. It was found that erosion of the nozzle is very low with such multi-directionally reinforced carbon/carbon composites.

There exists also an alternative production method for carbon/carbon composites, namely the impregnation by CVD the so-called gas impregnation. That means the primary matrix and the filling of the pores are performed by a chemical vapour deposition. This was the first process applied for carbon/carbon composites, and is still applied for the production of airplane brakes. At first time airplane brakes from carbon/carbon composites were applied for the CONCORDE, a British/French Jet aircraft. Today it is applied in all military jets.

A French study concerning performance characteristics of these materials for jet planes shows C/C in its behaviour between steel and beryllium discs. Applications of C/C brakes in cars are beginning, especially in high speed cars.

If we compare the high temperature mechanical properties of carbon/carbon composites with conventional materials, we see that the high temperature limit is only reached by pyrolytic graphite, however, the strength in fibre direction is 4 to 5 times higher than that of pyrographite.

Also the fatigue behaviour isvery interesting for carbon/carbon composites. Unidirectional reinforced materials with a density of only 1.6 g/cm^3 withstand an alternating flexural stress of 400 MN/m^2 after 10^7 load cycles.

It was mentioned before that in industrially produced carbon/carbon composites bulk density can reach 1.9, and in special cases up to 2 g/cm^3.

The strength properties increase with the density. In an application as in the space shuttle or in rocket nozzles mainly the thermal behaviour is important. In this case, the high density is absolute inevitable.

The impact strength of carbon/carbon composites was found to show a maximum with 20 % porosity.

Impact behaviour is very important for all applications of carbon/carbon composites, especially in space because of the danger of impact by meteorites. Impregnation by a polymer can perhaps help, but must be repeated before re-application.

Newest results which we have presented at the Carbon Conference in Philadelphia show the flexural strength of a carbon/carbon composite after four impregnation and recarbonization cycles with 1000 MN/m^2. This strength can be considerably improved up to 1500 MN/m^2 by only one final impregnation with an epoxy resin without carbonization, which fills the pores and thus the notches for the brittle fracture of the carbon/carbon composites. Perhaps such finishing could be a way to prepare carbon/carbon composites for a broader application field.

3.2. Application of carbon fibres as biomaterial

It has been reported since years that carbon is an extremely biocompatbel element. Application was studied for replacement of teeth, the repair, stretching and extension of bones, for replacement of joints and of heart valves. Pioneer in this field was obviously the CARDIFF team in England, and especially Professor D H R. JENKINS in the University of Wales.

Living tissue can grow surrounding carbon fibres. No inflammation or early signs of rejection is apparent in the healthy tissue. This observation was used to try a replacement of ligaments and tendons.

First series of experiments, the tendon Achilles of a serie of sheep was escised from musculotendenous junction to insertion of os calcis and replaced with a double-plaited strand of carbon fibre. The lower limb was not immobilised in any way after implantation. Within a few days the animals were able to bear weigth and within three weeks were able to run and walk normally. Within six months of implant the carbon had become totally buried in new tendon-like tissue whichgradually took on physiological functions and acquired a normal anatomical shape. Within one year a new tendon Achilles had been induced equivalent in every way to the untreated tendon.
We have performed similar experiemtns with sheeps and dogs in Germany in cooperation with the Orthopaedic Clinic in Ulm.

According to all experiences with animals, the knee ligaments appeared as most promising first application.

The technique was transferred to humans. The CARDIFF team New Wales has successfully replaced the anterior cruciate ligament in humans with chronic ligament instability, and the medial and lateral collateral ligaments of knee in patients with grossly unstable knees. The cronically unstable ankle has been successfully remedied by replacement of the deltoid ligament.

Other clinical applications have been the reinforcement of the distal-ulnar joint for chronic radio-ulnar sub-subluxation, realignement of the shoulder capsule. In all cases, the initial findings on animals have been closely reproduced.

According to my last informations there are four groups working in the world on application of carbon fibres as ligaments or tendons in human medicine: Professor JENKINS in Cardiff, Professor BURI in Ulm, Professor STROVER in Johannesburg, and the group of ALEXANDER/WEISS in New Jersey, USA. The first two groups have performed hundreds of successfull implantations already on knees and ankle joints.

The main differences in the application between the several groups have to be seen in the fixation of the carbon fibres or carbon textiles. The most advanced technique seems to us is the ingrowth of the carbon materials into the bone.

The excellent compatibility of carbon materials with the bone recommends carbon fibre reinforced materials as bone plates in osteo synthesis or in replacement of the hip joint. The last one is one of the most important problems in human medicine today. Model parts made from 3-dimensionally reinforced carbon/carbon composites are developed for replacement as alternative for the today used metal prosthesis, which are applied with a limitation of resistance time of average four years only. A first step in this direction the use of carbon materials as hip joint prosthesis has been done by the so-called WAGNER prosthesis which uses fine grained graphite and siliconcarbide impregnated graphite as gliding parts for this hip joint. First operations (up to 20) have been performed successfully in Germany during last year. It is hoped that also the full carbon hip joint prosthesis will be introduced in the near future.