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Processing and uses of carbon fibre reinforced plastics

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Contents

Processing and uses of carbon fibre reinforced plastics

Herbert Heißler

The development of carbon fibres has meant a most interesting addition to the group of materials known as fibre reinforced plastics. Following the introduction of the first carbon fibres in the late sisties, made in small amounts and sold at exceptionally high prices (around DM 3000,– per kg), the importance of this new fibre for the development of reinforced plastics was soon realised – especially for making high quality lightweight components [1].

In the early seventies, carbon fibres were being made from polyacrylonitrile as well as from regenerated cellulose (rayon). Today, rayon has been given up almost completely but pitch-like, bituminous products are becoming increasingly important for making carbon fibres [2].

In the early days, carbon fibres were available exclusively as rovings and this forced fabricators to limit their namufacturing processes to filament winding. For some years however, it has been possible to convert carbon fibres to high quality woven materials so that it has now become possible to produce flat components, as in GRP technology. Since carbon fibres are also available as prepregs – mainly epoxy-based – it has become possible for the fabricator to avoid the work-intensive wet laminating technique. For some years, too, chopped carbon fibres have been available, e. g. for reinforcing thermoplastics or for making thermoset moulding compounds.

Initially, the use of carbon fibre reinforced plastics (CRP) was confined almost exclusively to aerospace applications because of their high price. When, in the mid-seventies, large-scale plants for making carbon fibres became available in several countries, and carbon fibres were beginning to be produced in large amounts, prices dropped accordingly. This resulted in consideralbe expansion in the uses of CRP, especially in aircraft construction. Wide-body planes being developed, like the Boeing 767 and the Airbus A 310, will contain a wide range of CRP structural elements which will bring considerable savings in weight. For the Boeing 767, CRP components with a variety of functions are scheduled, weighing a total of 420 kg [3].

Another interesting field of application for CRP components is in transportation, especially in motor vehicles and rolling-stock. Typical examples include Cardan shafts and leaf springs for cars and lorries, as well as bogie components for railway waggons.

Considerable amounts of carbon fibres have been used in recent years for making a wide range of sports articles, mainly golf clubs. Also worth mentioning are boatbuilding and glider construction. CRP skis have also been developed.

There has also been growing interest in the use of CRP for industrial applications. Although the use of carbon fibres in any quantity has so far been confined to special fields such as the production of pressure tanks or centrifuge rotors, the use of CRP especially for general industrial applications is expected to increase very considerably in future.

Summerising, we can say that the development of CRP, regarded as a material, has come to an end and that the next phase, namely its introduction into a wide range of industrial fields has now begun.

The reasons include the following:

> The capacity plants for the large scale production of the different types of carbon fibres are now available, and considerable capacity increases are scheduled for the next few years [4].

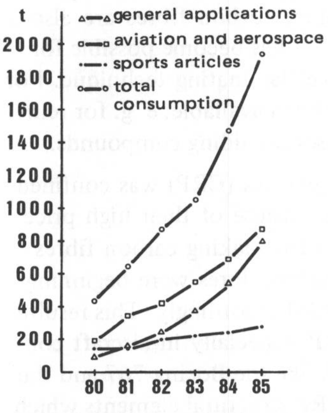

Fig. 1. Annual consumption of carbon fibres, as estimated by manufacturers for various applications.

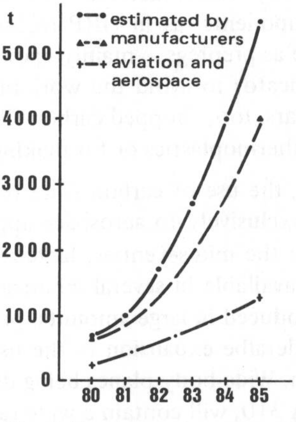

Fig. 2. Total annual consumption of carbon fibres. Manufacturers' estimates as well as for aviation and aeraspace applications.

Because of the greatly increased demand and the fact that plants are working to capacity, the price of carbon fibres has dropped to a sufficiently low level to enable CRP to be used in many different fields. Carbon fibre prices are still following a downward trend [4].

The question now ist what forecasts can be made for the next 3 – 5 years with regard to carbon fibre production and price developments. Estimates by some major producers are shown in figs. 1 and 2.

Annual production and consumption of carbon fibres up to 1985

Such estimates naturally show considerable variations, both as regards total quantities as well as consumption in the different fields. It is estimated that production capacities in the USA will increase about tenfold within the next five years, whereas those in Japan and Europe will only quadruple.

There are estimates for carbon fibre consumption which state that about 2600 tonnes will be used in 1985, of which 2000 tonnes will be used in the USA. Aviation aerospace applications take up about half the total usage, i. e. around 1300 tonnes, which represents a rate of increase of 500 – 600 % compared with 1980. The main share of 900 tonnes applies to the USA. Very considerable increases in consumption are expected in the car industry although it should be mentioned that at the moment CRP components such as leaf springs and Cardan shafts are still in the development or testing phase. Another point is that economical production processes, machines and epuipment for the large-scale manufacture of such components must first be developed and tried out. Estimates indicate that this phase will have been completed by 1985 at the latest.

Estimates also predict a considerable carbon fibre consumption for general industrial applications, spread over a large area and including fast moving components such as rotors for centrifuges, components for textile, printing and papermaking machines, clutch and brake discs, components for moving aerials and for crane installations.

A large proportion af total carbon fibre consumption will be used for sports articles, primarily golf clubs and boat masts, as well as components for gliders, fishing rods, skis etc. [4].

Price situation up to 1983, fig. 3

The predicted enormous rates of increase for production and consumption of carbon fibres are having a lasting effect on price developments, and it is

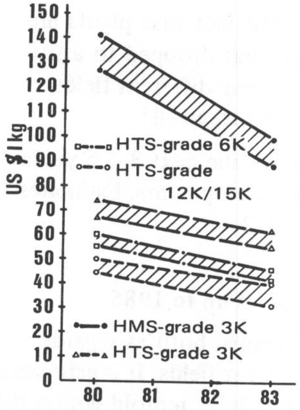

Fig. 3. Estimated price development for carbon fibre rovings for a 2000 kg order.

expected that this downward in the price of carbon fibres will be maintained also after 1983.

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High strength carbon fibres based on polyacrylonitrile: available forms and properties in CRP composites

Philip G. Rose

The hopes expressed during the first VDI Conference on carbon fibre reinforced plastics [1] for the continuing development and use of PAN-based carbon fibres have been realised. One can in fact say that the optimism expressed at the time was somewhat guarded. A turnover growth of about 40 % p. a. and constantly falling prices are proof of a true material revolution [2]. This development is shown graphically in fig. 1 for the normal strength qualities NF 3 and NF 6, with 3000 and 6000 separate filaments per roving respectively. The demand by 1990 is expected to be about 6 000 tonnes p. a. at a price of about 30 DM/kg. This would mean that CRP would be absolutely competitive with light metals, especially when one considers that 1 kg CRP is equivalent to almost 2 kg aluminium from the point of view of performance. One can even use 1 kg CRP in place of 5 kg steel in components where stiffness is important. It is likely therefore that during the nineties, CRP will be used in general machine and vehicle construction.

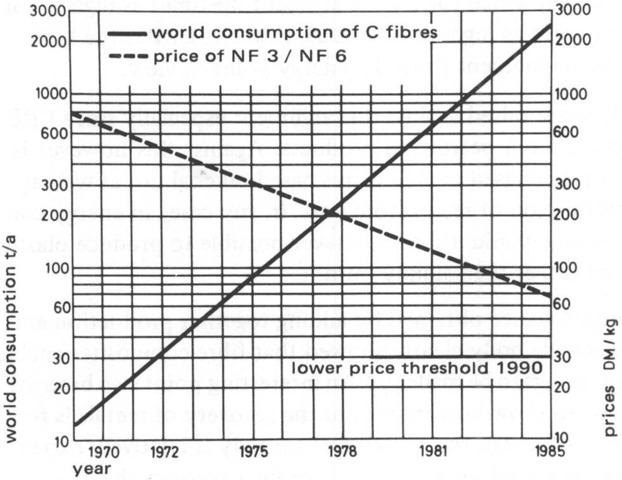


Fig. 1. Development of world consumption and price of carbon fibres based on PAN.

The decisive factor underlying the choice of PAN-based carbon fibres in the present stage of development is not, of course, the price but the savings in weight that can be achieved. This is an important consideration especially in the aviation and aerospace industries, where designs have already reached the limit of performance of light metal alloys. Nowadays, no aircraft is designed without CRP materials. In civil aircraft construction the saving in weight means greatly reduced fuel costs whilst in the military field, CRP increase performance [3]. That the aircraft industry is ahead in the development of CRP as well as other carbon fibre reinforced materials such as ceramics and metals is therefore hardly surprising. Other branches of industry will inevitably follow. It has already been established that manufacturing costs for CRP components can be appreciably lower than those for aluminium.

The important factor in this new age of rising energy costs and dwindling energy resources is not only the saving of fuel by means of lighter cars and aircraft, but also the use of materials whose production, fabrication and finishing require less energy. Here, it is useful to compare the energy contents of potentially interesting materials. Kenward [5] has compared plastics with glass and metals on the basis of the crude oil equivalent and thus the energy cost. His findings, completed by the relevant figures for GRP, carbon fibres and CRP, are shown in table 1.

The most favourable figures are those of GRP. From the point of view of specific rigidity however, which for CRP is at least four times as high as for GRP and more than twice as high as for metals, table 2, CRP is the best material available at the moment from the energy point of view.

Obviously, objections are raised against this argument especially since CRP materials are obtained from petroleum products. Against this however is the development of pitch-based carbon fibres based on coal tar, as well as methods for the production of resins from coal. In any case, an energy conscious material economy would use oil wherever possible to produce plastics and fibre composites rather than simply burn it.

A study of the energy balance obtained by adding together production and running costs for a vehicle body clearly showed that fibre composites enable considerable energy savings to be made [6]. An interesting point also brought out by this study was to show how important the recovery of metals is for their economical use. Although the rolled steel carbody is relatively expensive from the energy point of view, even taking into account the energy value of the scrap metal, the cost of aluminium and CRP would be com-

Table 1. Comparison of energy prices for the most important machine construction materials.

Werkstoff	Density g/cm³	Oil tonnage equivalent by weight			Energy price kJ/cm³ material
		for raw material	for conversion	for the material	
Aluminium	2,7	–	5,6	5,6	665
Steel	7,8	–	1,0	1,0	385
Synthetic resins and polymers	1,1	1,3	1,88	3,18	150
Glass fibre	2,6	–	0,45	0,45	50
Carbon fibre (PAN-based)	1,8	3,0	3,6	6,60	5,25
Carbon fibre (pitch-based)	1,8	1,5	2,0	3,50	277
CRP (60 % v/v fibres)	2,0	0,52	1,02	1,54	134
CRP (PAN-based with 60 % v/v fibres)	1,6	2,32	2,55	4,87	365
CRP (pitch-based with 60 % v/v fibres)	1,6	1,42	1,95	3,37	239

Table 2. Mechanical properties of CRP (high strength and high modulus fibres) and other materials (fibre orientation 0°, 45°, proportion 50 : 50).

Mechanical properties	Wood (pine)	Aluminium alloy (Dural)	Titanium alloy (TiA 16. Va 4)	Steel	CRP $\vartheta = 0°, 45°$ 50 : 50 $V_f = 60\ \%$	CRP laminated like CRP $V_f = 60\ \%$	
						HT	HM
Tensile strength or proportional stress (N/mm^2)	100	350	800	1100	720	900	720
Elastic modulus (N/mm^2)	12×10^3	75×10^3	110×10^3	210×10^3	30×10^3	88×10^3	120×10^3
Density (g/cm^3)	05	2,8	4,5	7,8	2,1	1,5	1,6
Specific strength or tenacity (km)	20	13	18	14	34	60	45
Specific elastic modulus or elongation (km)	$2{,}4 \times 10^3$	$2{,}7 \times 10^3$	$2{,}4 \times 10^3$	$2{,}7 \times 10^3$	$1{,}4 \times 10^3$	$5{,}9 \times 10^3$	$7{,}5 \times 10^3$
Torsion modulus (N/mm^2)	–	28×10^3	42×10^3	81×10^3	23×10^3	23×10^3	30×10^3

parable if one only considered the recovery of the aluminium. It is therefore to be expected that steel will be replaced in ever increasing amounts by aluminium for vehicles, and by CRP in those components for which aluminium does not have the required properties.

Every material will have its ecological niche in the economy of the future. Because of its high strength, lower energy requirements and inexpensive methods of fabrication, CRP will here play a very important part.

Manufacture

Polyacrylonitrile (PAN) is noted for the following characteristics as a raw material for the production of carbon fibres:

> It can be spun under very clean conditions into highly oriented, very fine fibres.
>
> Oxidative heat treatment produces a stabilised fibre with the axially parallel molecular orientation of the original fibre. This preferential orientation is maintained during coking and determines the high elastic modulus of the fibre.
>
> Compared with other oriented fibres (e. g. viscose, PVA and PA) the carbon yield of PAN is very high, with 55 % w/w.
>
> High strength carbon fibres (at present with tensile strengths of around 4 500 N/mm^2) can be made from PAN, with a relatively high elongation at break of 1.5 % without having to manipulate the fibre during coking – something that appears to be not yet possible with pitch.

The chemistry of the transformation of PAN into the carbon fibre structure is shown below. For details of the reactions see [7 to 13].

During reactions II and III it is necessary to keep the PAN fibre under accurately controlled tension. Since both mechanisms are very strongly exothermic, they must be controlled so that the fibre will not break and yet is stabilised as quickly as possible. The zipper reaction to produce polyimine (II) can be catalysed with Lewis acids [12, 14 15]. Tension suppresses this reaction [16].

The oxidation reaction is regulated by diffusion so that it necessitates the use of a very fine fibre as starting material because the oxidising agent must be able to diffuse uniformly. An extreme example of insufficient oxidative stabilisation is shown in figs. 2 and 3 [17].

Fig. 2. Structure of core and outer layer of an oxidised, PAN-based fibre (60 den).

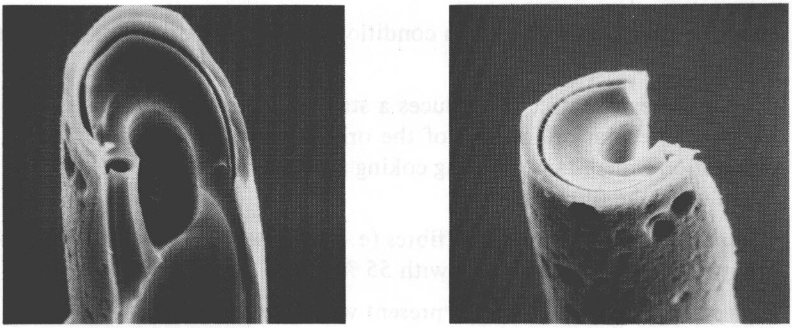
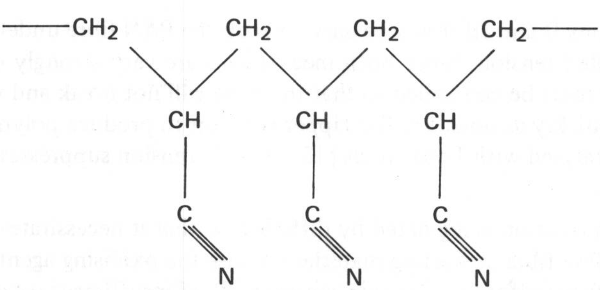


Fig. 3. Hollow carbon fibre after coking and melting of the core.

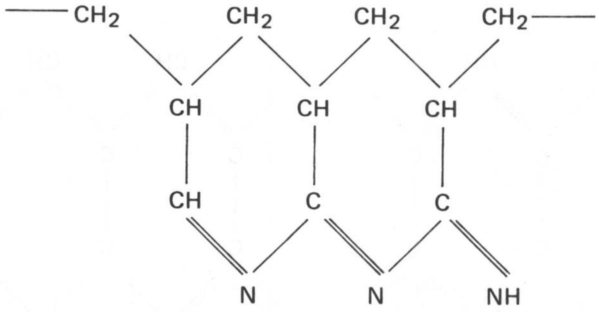
Reaction schemes

I PAN



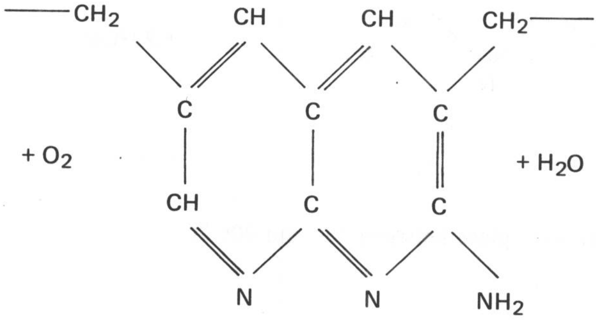
Oriented linear polymer, stable up to 180 °C

II Zipper reaction
180 – 250 °C



Oriented ladder polymer, stable up to 345 °C [9]

III Oxidation of II
to 350 °C

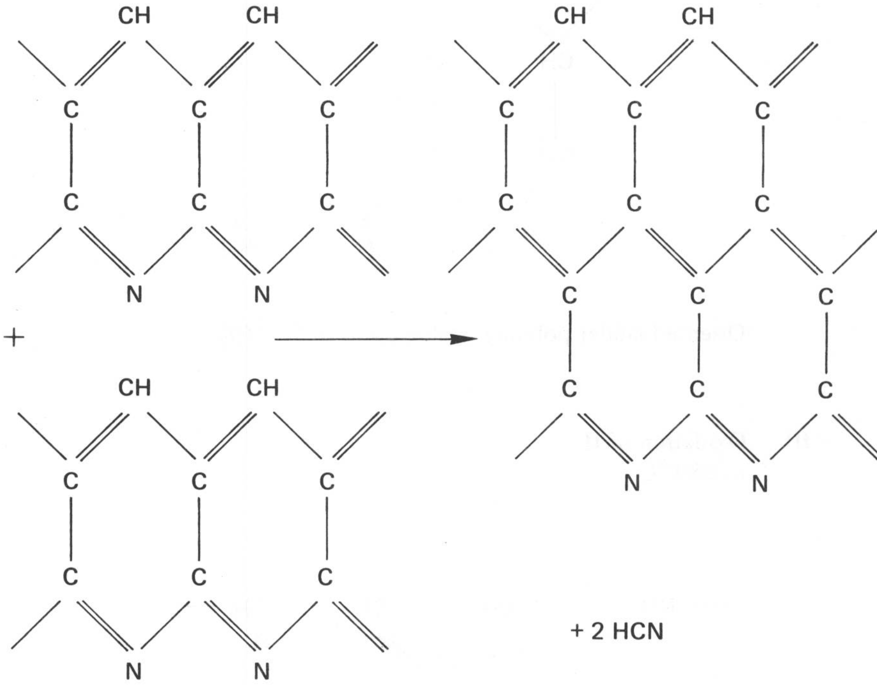


Cyclised ladder polymer which will no longer fuse

Coking possible without tensile stress

IV Condensation of III
i. e. coking up to 1500 °C

a)



Reaction takes place between 350 and 900 °C