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by

Zbigniew Guzek

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CARBON FIBRES IN REINFORCED PLASTICS

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1. Introduction

An elongated fibrous shape of a reinforcing agent in composite materials is one of the most desirable forms, since it permits imparting directional properties to the composite material.

The most often used reinforcing fibers are glass fibers of various types, such as E, S and D. Technical parameters of glass fibers, according to Mettes /1/, are shown in Table 1. In addition to glass fibers, which have amorphous structure, some crystalline fibers are also used as reinforcements. They can be whiskers, hairy monocrystals, as well as polycrystalline oxide fibers, metal fibers, and others.

Owing to their more perfect structure, crystalline materials permit obtaining fibers with high mechanical strength. This fact can be seen in technical parameters of whiskers (Table 2), which are devoid, to a large degree, of structural errors and surface imperfections /2/. However, the range of applicability of such hairy fibers is limited, because of technical difficulties in their production and also on account of the complicated technology of placing very small whiskers (13×10^{-6} to 25×10^{-4} cm) in ordered manner in a material to be reinforced.

In Table 2 special attention is drawn by outstanding strength parameters of graphite (position 5) and its low density and great resistance to high temperatures. Carbon, both in the form of whiskers and also polycrystalline fibers, has large potential of applications in reinforcement technology for composite materials.

Figure 1 shows specific strength (ratio of the mechanical strength of material to its density) and specific modulus of elasticity (ratio of the modulus E to the density) for various reinforcing fibers, including carbon fibers, according to Taprogge /4/. Similar values are reported by Gill /5/.

The more graphitized carbon fibers obtainable at elevated temperatures are called graphite fibers by some authors. Carbon fibers and graphite fibers distinguish themselves favorably among conventional reinforcing materials not only by their tenacity, but also by low density, resistance to the action of environment, and preservation of properties at high temperatures.

2. Production of carbon fibers

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Beginnings of the production of carbon fibers are connected with the name Edison. He carbonized materials containing cellulose and in appropriate chambers was obtaining carbon filaments of shape given to the carbonized initial material. Other methods of obtaining carbon in the form of fibers at the beginning of 20-th century consisted of spraying cellulose dissolved in zinc chloride into a hardening bath, or placing carbon on a fibrous

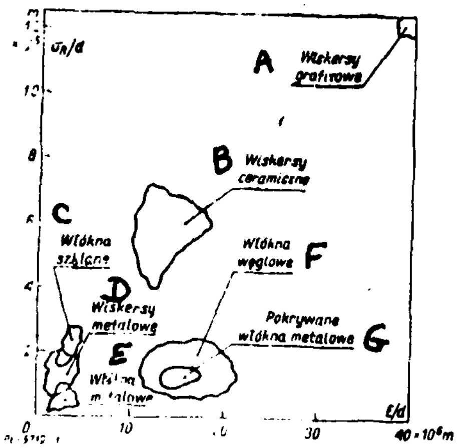
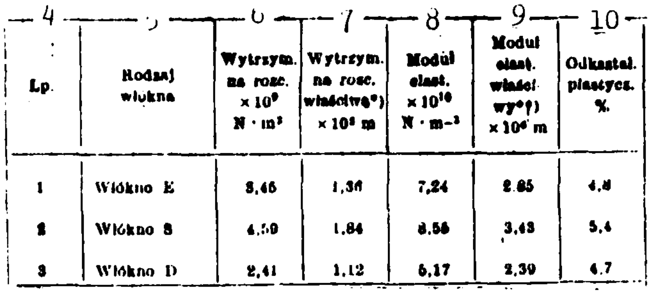


Figure 1. Specific tenacity σ_R/d and specific modulus of elasticity E/d of various reinforcing materials:

A - graphite whiskers
B - ceramic whiskers
C - glass fibers
D - metal whiskers
E - metal fibers
F - carbon fibers
G - coated metal fibers



4	5	6	7	8	9	10
Lp.	Rodzaj włókna	Wytrzym. na rozc. × 10^9 N · m^2	Wytrzym. na rozc. właściwa*) × 10^5 m	Moduł elast. × 10^{10} N · m^{-2}	Moduł elast. właściwy**) × 10^6 m	Odkształ. plastycz. %
1	Włókno E	3,46	1,36	7,24	2,85	4,8
2	Włókno S	4,59	1,84	8,56	3,43	5,4
3	Włókno D	2,41	1,12	6,17	2,39	4,7

Table 1. Mechanical strength, modulus of elasticity and plastic deformation of glass fibers.

Horizontal headings: 4/Consecutive number; 5/type of fiber; 6/elongation strength x 10^9 N.m^{-2}; 7/specific* elongation strength x 10^5 m; 8 modulus of elasticity x 10^{10} N.m^{-2}; 9/specific** modulus of elasticity x 10^6 m; 10/plastic deformation %

Vertical headings: 1 - Fiber E; 2 - Fiber S; 3 - Fiber D

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*) Specific strength - strength in relation to density σ / d in m

**) Specific modulus of elasticity - E / d in m

9 Lp.	Materiał	11 Temp. °C	12 Wytrzym. na rozc. · 10^9 $N \cdot m^{-2}$	13 Wytrzym. na rozc. właściw. × 10^5 m	14 Moduł elast. × 10^{10} $N \cdot m^{-2}$	15 Moduł elast. właściw. × 10^6 m
1	Tlenek glinu	2082	13,8 – 27,6	3,5 – 7,1	68,9 – 24,1	17,67 – 61,85
2	Azotek glinu	2199	1,38 – 20,7	1,1 – 6,3	34,5	10,45
3	Tlenek berylu	2549	13,8 – 19,3	7,7 – 10,7	68,9	38,27
4	Węglik boru	2449	6,9	2,7	41,8	17,92
5	Grafit	3602	20,7	9,2	97,9	43,51
6	Tlenek magnezu	2799	24,1	6,7	31,0	8,00
7	Węglik krzemu	2316	6,9 – 34,5	2,2 – 11,0	48,1	15,11
8	Azotek krzemu	1899	3,4 – 10,3	1,1 – 3,2	37,9	11,81

Table 2. Elongation strength, modulus of elasticity and melting temperature of whiskers from various materials /3/.

Horizontal headings: 9 / Consecutive number; 11 / temperature °C; 12 / elongation strength x 10^9 $N.m^{-2}$; 13 / specific elongation strength x 10^5 m; 14 modulus of elasticity x 10^{10} $N.m^{-2}$; 15 / specific modulus of elasticity x 10^6 m

Vertical headings:

1 - Aluminum oxide
2 - Aluminum nitride
3 - Beryllium oxide
4 - Boron carbide
5 - Graphite
6 - Magnesium oxide
7 - Silicon carbide
8 - Silicon nitride

base material through which electric current is passed in a hydrocarbon atmosphere.

The obtained carbon fibers had good electrical properties, taking into consideration applications for which they were intended. However, they could not become reinforcing materials because of their brittle nature. In the course of work to improve properties of these carbon fibers much has been learned about single parameters of production process, such as the quality of initial material (precursor), temperatures of the consecutive stages of decomposition, rates of processes, atmosphere, catalytic agents, etc.

2.1. Low-strength and low-modulus fibers from cellulose

At the beginnings of production of carbon fibers the most often used initial materials were cellulose and artificial silk. They allowed to obtain about 15% carbon in the process of pyrolysis.

The process of carbonization of cellulose has not been as yet properly explained /6/. From their infrared studies Tang and Bacon /7/ establish the following stages of decomposition:

I. Desorption of water, occurring at temperatures 25-150 °C,
II. Dehydration of cellulose itself, at 150-240 °C,
III. Thermal rupture of chain and other C-O bonds, and formation of C-C bonds through the reaction of free radicals , occurring at 240-400 °C,
IV. Aromatization above the temperature 400 °C.

The carbonizing fibers do not lose their original shape. Specific properties can be obtained by carrying out properly the process of carbonization. According to U.S. Patent 3 100 1[illegible]2 the proper decomposition in the process of production of graphite fibers is assured by: a protective atmosphere and the defined rise of temperature /8/:

- at the rate of 10-50 °C/hour in the temperature range from 100 to 400 °C,
- at the rate of 100 °C/h in the range 400 to 900 °C,
- further heating up to 3000 °C till graphitization occurs.

Thinner fibers exhibit a considerably higher strength; this is explained by a relatively easier evolution of volatiles from the precursor without disturbing the structure. An increase of strength of the produced carbon fibers is obtainable by means of increasing the yield of carbon in the process of carbonization by introducing catalysts into the protective atmosphere. Such catalysts may be in the form of oxygen-free acids, e.g. HCl /9/.

2.2. High-modulus fibers from cellulose

Carbon fibers obtained by the method described in the preceding section (2.1) do not have a high mechanical strength and stiffness. When compared with glass fibers, carbon fibers have barely similar stiffness, and their elongation strength reaches only 20% elongation strength of glass fibers. Structural studies have shown considerable imperfection of fibers obtained in this way. It is found that graphite layers, which should be placed in the fiber parallelly to elongated axis, do not fulfill this condition and show large deviations and faults. In addition, studies using an electron microscope have revealed a considerable number of pores of large dimensions, above 100 Å. Hence, the fundamental condition for improving strength parameters of carbon fibers is an improvement of their structure. This conclusion was confirmed by introducing the step of stretching (drawing) in the process of production of carbon fibers, the step which provides conditions for obtaining a more perfect structure. When the fiber was extended 7%, the modulus of elasticity increased from 1.8×10^{10} N.m^{-2} to 5.5×10^{10} N.m^{-2}, and at the extension of 16% it rose to 57.1×10^{10} N.m^{-2}. It is obvious that orientation of the layers of graphite crystals has the decisive effect upon the modulus of elasticity of fibers.

There are several ways in which the process of graphitization with simultaneous drawing (stretching) of carbon fibers can be accomplished at a temperature near 3000 °C /10/. The fiber can be passed through a refractory graphite pipe, or it can be heated directly by passing electrical current through it. A variable controlled drawing of fibers is achieved by application of different velocities of unwinding and winding, coupled with pulling action of suspended weights.

The application of tension to the fiber at high temperatures results in sliding of the formed graphite crystals along each other, increasing thus the degree of their orderly placement. The higher is this extension, the more regular is the structure, the lower is the porosity, and the higher is the modulus of elasticity. Artificial silk appears to be the best cellulosic precursor.

Among other materials used successfully as precursors in the technology of making carbon fibers the leading position is taken by polyacrylonitrile (PAN).

2.3. Carbon fibers from PAN

During the course of the search for a suitable raw material for carbon fibers of high mechanical strength it was found that a copolymer containing at least 30% polyacrylonitrile (PAN), heated to the temperature about 350 °C in oxidizing atmosphere and then to 800 °C or higher, yields a carbon or graphite product with the shape of initial material /11/.

Shindo has shown in his studies /12/ that starting with PAN one can obtain carbon fibers with modulus of elasticity $F = 16.9 \times 10^{10}$ $N.m^{-2}$, and at the same time the yield of carbon is 50% and not 15% as it occurs in the case of use of a cellulosic precursor. These results can be obtained without the application of tension (drawing).

Introduction of a preliminary heating in N_2 atmosphere and introduction of a slow rate of temperature rise enabled to reduce losses of carbon and to preserve longer chains. In this way, starting with homopolymer and heating fibers to 1000 °C one can obtain elongation strength 0.75×10^9 $N.m^{-2}$. This strength is 0.99×10^9 $N.m^{-2}$ when copolymer is initially used.

Additional steps, such as heating PAN in air atmosphere for 24 hours at the temperature 290 °C, heating in oxygen-free atmosphere up to 1000 °C, and subsequently graphitization at the temperature 2500 °C, enable to obtain continuous fibers with tensile strength 1.75×10^9 $N.m^{-2}$ /13/.

As is known, graphite monocrystals assume closely packed structure in hexagonal system, and have the density 2.25 g/cm^3. The distance between basic planes is 3.354 Å. The carbon obtained in the process of carbonization carried out at high temperatures is packed less densely, and the distances between planes are irregular and higher than 3.354 Å. This irregular structure (turbostratic) of carbon undergoes improvement in the process of graphitization at the temperature 2000-3000 °C.

Carbon fibers arising from PAN precursor are round and are not twisted. The density is of the order of 1.32 up to 1.96, hence approaches the theoretical value /14/. On the basis of the above discussion it can be assumed that the basic changes in the process of formation of carbon fibers from PAN occur under the influence of temperature in the initial and final stages of carbonization.

2.3.1. Changes occurring during decomposition of PAN

PAN fibers are made of material consisting of a chain of repeated elements with active CN groups and triple bonds. On heating, PAN forms a ladder polymer. The intragroup crosslinking causes that the polymer is more stable and does not melt easily /15/.

Heating above 200 °C triggers the occurrence of a number of reactions involving the evolution of HCN, NH_3 and other volatile compounds. At about 220 °C oxygen becomes built into the structure, and its entrance is connected with crosslinking. 323 The amount of entering oxygen is 8-10%. During the oxidation water volatilizes causing that the percent content of carbon increases from 30 to 45%.

When the tension is applied at the stage of oxidation and oxygen-crosslinking between molecular chains, these chains are taut and oriented parallelly to the fiber axis, so that even after removal of elongating tension in later periods of heating the proper orientation is retained.

Kesatochkin and Grassi /16-17/ show a number of other reactions occurring in the process. However, the most important reaction remains the oxygen-crosslinking.

In the process of carbonization the fiber attains the well developed ring structure of carbon, with small crystals oriented along the axis of fiber, which provides, as said before, a large mechanical strength and stiffness.

Values of these parameters may undergo further changes under the action of high temperatures. These processes consist primarily of graphitization and recrystallization, leading to an increase of stiffness of fibers. For it was found that further heating of carbonized fibers with already developed and oriented

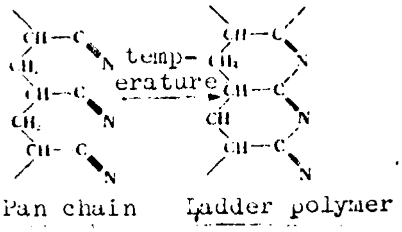

Figure 2. Formation of ladder polymer from PAN chain

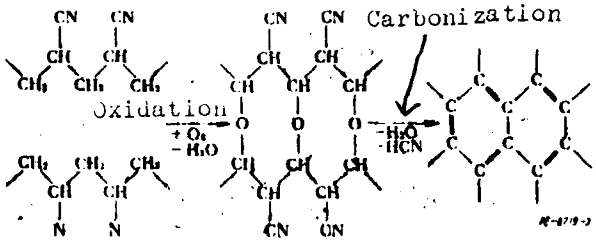

Figure 3. Oxygen-crosslinking and carbonization of PAN fibers

structure leads to an increase in the modulus of elasticity. On the other hand, the process of graphitization above 1600 °C is disadvantageous to mechanical strength. This strength suffers degradation up to the temperatures of the order of 2400-2600 °C where it undergoes a certain stabilization. The dependence of mechanical strength on temperature in the region of graphitization (1200-3000 °C) is shown in Figure 4 according to Gill /15/.

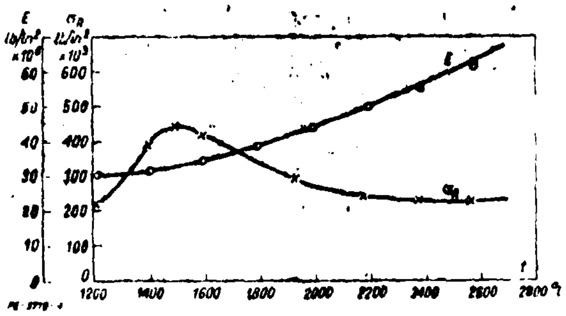

Figure 4. Changes in mechanical elongation strength σ_R and in modulus of elasticity E of heated carbon fibers from PAN

The course of curves $\sigma_R=f=(T)$ and $E=f(T)$ indicates that one can control properties of fibers to quite a great extent by choosing appropriate conditions of the process of heating.

3. Physical and chemical properties of carbon fibers

3.1. Physical properties

Technical data concerning the properties of carbon fibers are rather scant and often controversial.This is understandable in view of a rather short history of fibers as reinforcing material and of the fact that the development work on these fibers is still going on.

Table 3 shows properties of various carbon fibers. For comparison, this Table contains also relevant data concerning other reinforcing materials.

Table 3. Physical properties of carbon fibers and other reinforcing materials

21 Lp.	22 Materiał wzmacniający	23 Gęstość g·cm⁻³	24 Wytrzymałość na rozc. ×10⁹ N·m⁻²	25 Moduł elastyczn. ×10¹⁰ N·m⁻²	26 Wytrzymałość na rozc. właśc. ×10⁵m	27 Moduł elastyczn. ×10⁶m
1	Włókno węgl. WYB 125	1,32	0,66	4,2	0,46	3.16
2	Włókno węgl. GRAFIL HM	–	1,70	36,0	–	–
3	Włókno węgl. GRAFIL HT	–	2,60	20,8	–	–
4	Włókno węgl. GRAFIL A	–	2,30	21,6	–	–
5	Włókno węgl. SIGRAFIL HM	1,83	1,37	31,3	0,76	17.20
6	Włókno węgl. THORNEL 10	1,33	1,15	9,6	0,86	7.22
7	Włókno węgl. THORNEL 25	1,42	1,24	16,6	0,87	13,10
8	Włókno węgl. THORNEL 40	1,66	1,75	[illegible]	1,11	17 00
9	Włókno węgl. THORNEL 50	1,67	2,16	36,2	1,31	23,47
10	Włókno węgl. THORNEL 75	1,82	2,64	56,4	1,45	29 80
11	Włókno węgl. MODMOR I	1,99	1,76	[illegible]	0,86	21,21
12	Włókno węgl. MODMOR II	1,74	2,46	24,6	1,41	14.16
13	Włókno węgl. REFIL KHW-18	1,70	0,9	–	0 53	–
14	Włókno szkl. E	2,54	3.45	7,2	1 38	2.85
15	Włókno szkl. S	2,49	4,59	8,6	1,81	3,43
16	Drut aluminiowy	2,71	0,29	6.9	0,11	2.55
17	Drut berylowy	1,85	1.1	31	0.59	16.76
18	Drut wolframowy	19,30	2,9	34,5	0,15	1 79
19	Drut stalowy	7,90	2 4	29	0,30	3 67
20	Drut kombinowany bor na wolframie	2,62	3.17	42,1	1.21	13,8

Table 3 (contd)

Horizontal headings: 21 /Consecutive number; 22 /Reinforcing material;
23 Density g.cm^{-3}; 24 /Elongation strength x 10^7 N.m^{-2};
25 Modulus of elsticity x 10^1 N.m^{-2}; 26 /Specific elongation
strength x 10^5 m; 27 /Specific modulus of elasticity x 10^6 m

Vertical headings:

1 - Carbon fiber WYB-125
2 - Carbon fiber GRAFIL HM
3 - Carbon fiber GRAFIL HT
4 - Carbon fiber GRAFIL A
5 - Carbon fiber SIGRAFIL HM
6 - Carbon fiber THORNEL 16
7 - Carbon fiber THORNEL 25
8 - Carbon fiber THORNEL 40
9 - Carbon fiber THORNEL 50
10 - Carbon fiber THORNEL 75
11 - Carbon fiber MODMOR I
12 - Carbon fiber MODMOR II
13 - Carbon fiber REFIL KBW-13
14 - Glass fiber E
15 - Glass fiber S
16 - Aluminum wire
17 - Beryllium wire
18 - Tungsten wire
19 - Steel wire
20 - Composite wire
beryllium on tungsten

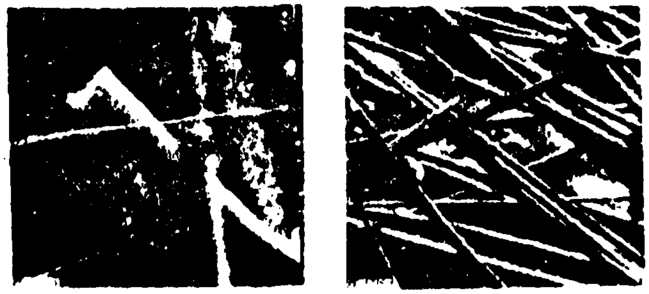

Figure 5 (left). Carbon fibers ZEFIL KBW-13 in the picture of secondary electrons; magnification 240X

Figure 6 (right). Carbon fibers ZEFIL KBW-13 in the picture of secondary electrons; magnification 960X

Figures 5 and 6 show fibers ZEFIL KBW-13 under magnifications 240X and 960X. They were obtained by means of an X-ray microanalyzer IXA-5A from JEOL company. Pictures of secondary electrons show clearly various protruberances, bubbles and uneven forms on surfaces of fibers. These imperfections are reflected in low mechanical properties of these fibers (Table 3, Position 13).

Comparison of physical features of reinforcing materials, presented in Table , enables one to conclude that:

- the density of carbon fibers is several times lower than that of reinforcing wires; it is also about 40% lower than the density of glass fibers;

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- the elongation strength of carbon fibers is about half of that of glass fibers; it is, however, comparable to that of metallic fibers;

- specific elongation strength of carbon fibers is within the range of the specific elongation strength of glass fibers type E. This strength is several times higher than the specific strength of metal wires;

- the stiffness of carbon fibers is outstandingly large. The elasticity modulus E of carbon fibers is 5-7 times larger than that of glass fibers, and by about 50% higher than the modulus of metal wires. This advantageous feature is visible even more when comparing respective values of the specific modulus of elasticity;

- carbon (graphite) fibers distinguish themselves very favorably in their resistance to the action of high temperatures - see Table 4.

3.2. Chemical resistance

An important feature of carbon and carbon fibers is their chemical inertness. Up to the temperature 350 °C they are chemically resistant, with exception of strongly oxidizing agents. An important condition is to prevent contact of fibers with air.

Comparative studies of the effect of various chemical agents on carbon fibers, carried out by N.C.W. Judd /18/, confirm the large resistance of fibers. Mechanical parameters of fibers exposed to the long action of environment have not deteriorated to any large degree.

Table 4. Melting temperatures of various reinforcing materials

No.	Material	Melting (* softening) temp., °C
1	Glass type E	846*
2	Glass type S	970*
3	Glass type D	771*
4	Aluminum	660
5	Beryllium	1350
6	Tungsten	3410
7	Austenic steel	1539
8	Molybdenum	2625
9	Copper	1083
10	Graphite	3592

Similar results were also obtained in studies of resistance of English carbon fibers GRAFIL HM, GRAFIL HT and GRAFIL A to aggressive environment by G.L. Hart and G. Pritchard /19/.

Other properties of fibers are shown in Table 5.

3.3. Possible improvements of parameters of carbon fibers

The modulus of elasticity of commercially produced carbon fibers reaches the values 40-50 x 10^{10} $N.m^{-2}$. On laboratory scale values of the modulus come up to 70 x 10^{10} $N.m^{-2}$. The modulus of elasticity of graphite monocrystal in the direction of axis (a) amounts to 100 x 10^{10} $N.m^{-2}$. Hence, the margin of increasing values of the Young modulus is actually not so large.

Table 5. Other properties of carbon fibers from PAN

No.	Property	Carbon fiber High-modulus	 High-strength
1	Elongation (%)	0.5	1.0
2	Specific electrical resistance at 25°C (μΩcm)	775	1500
3	Coefficient of thermal expansion, 0-50°C ($10^6 \cdot {}^{\circ}C^{-1}$)	1.62 (negative)	0.78 (negative)

Theoretically, mechanical strength in bending should be $F/10$. In practice one obtains only $F/200$ or $F/100$ for high-strength fibers. An improvement of technical parameters of fibers should, therefore, be attempted in this direction. This work requires a better knowledge of the sources of defects in fibers, and also positive results in attempts to improve their surface.

4. Applications of carbon fibers. Conclusions

Main advantages of carbon fibers are: resistance to high temperatures, resistance to chemical action, high stiffness and low density. On the other hand, the shortcoming is their actual high price. One has to note, however, that a continuous although slow reduction in the price of carbon fibers is observed.

This gradual lowering of price is seen as a result of improvements in production methods as well as broadening of the spectrum of applications and increase in market demand.

In the initial period, carbon fibers were used exclusively in structures in which properties of composite materials were of paramount importance and the price did not play any role. We speak here about composite materials in cosmic (space) ships. Elements from materials with carbon fibers had maximal stiffness, were more resistant to the action of high temperature, and they considerably reduced the mass of structure. Carbon elements reinforced with carbon fibers were used in cosmic vessels (spaceships) also to utilize the phenomenon of ablation in the use of vehicle parts exposed to particularly high temperatures.

The next domain, in which carbon fibers were used to reinforce plastics, was aviation. The use of fibers was influenced by the necessity to increase the degree of flight safety.

Lightness combined with high strength paved the way for application of composite materials with carbon fibers in installations and machines for competitive sports.

Possibilities of application of composite materials with carbon fibers exist also in other areas, for instance in chemistry and electrotechnical industry. In chemistry, for instance, they could be used in construction of mixers and tanks, mechanically strong and resistant to corrosion.

In electrotechnology, it appears that carbon fibers could be used primarily as reinforcing material for metals, such as copper and aluminum, for aerial cables of high mechanical strength, for traction cables of fast electrical trains, and for fast-rotating parts of machines. In other applications, composites with carbon fibers may find applications in the construction of shielding and grounded protective covers, brushes, fast moving elements of computers, etc.

The present high prices of carbon fibers have restrictive effect on the broadening of fiber applications. It appears that a condition for considerable growth of interest in carbon fibers is at least tenfold reduction in their price.

This discussion on carbon fibers should be supplemented with the statement that, because of their specific character, these fibers do not present competition for the currently used fibrous reinforcing materials. But they are a valuable supplement for this group of materials, broadening the possibilities of creating composite materials with new properties.

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