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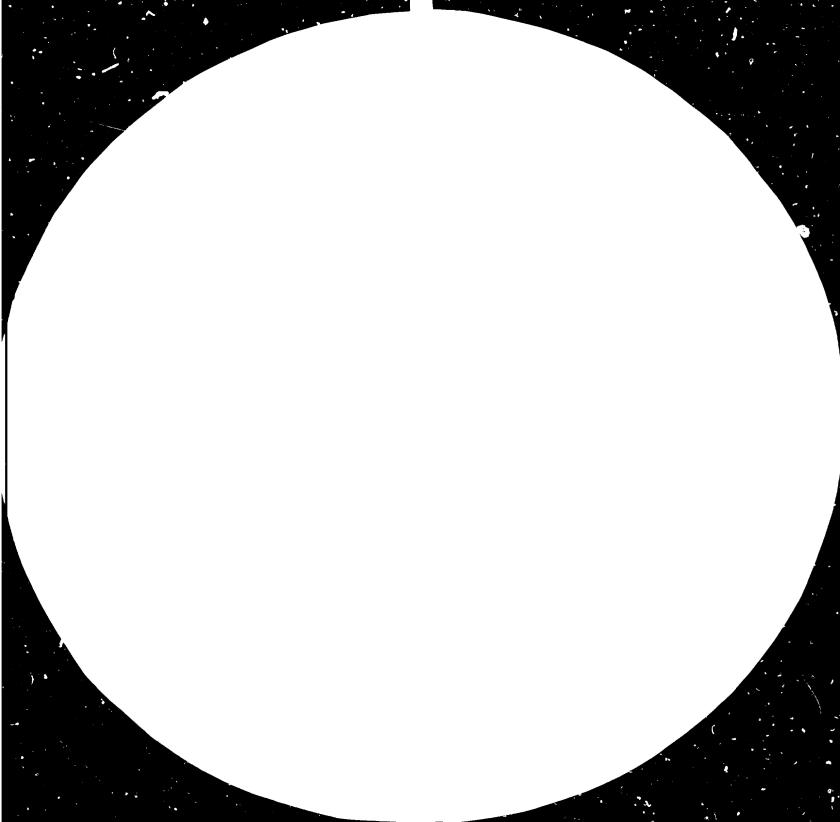
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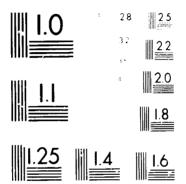
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INDUSTRIAL, MARINE, AND RECREATIONAL APPLICATIONS

OF CARBON FIBRES AND THEIR COMPOSITES*

by

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INTRODUCTION

These applications are generally considered together for nontechnical reasons. First, in selling the material as well as in making market assessments, one must address a diversity of manufacturers, instead of dealing with the relatively few hightechnology aerospace and automotive companies, which are in the forefront of materials' R&D. Secondly, the applications in the title sectors are generally much less weight-critical and much more cost sensitive. As a matter of fact, non-aerospace applications did not exist until the price of carbon fiber (CF) dropped below \$100/Kg in the early seventies. The current U.S.A. prices of the structural CF tow or yarn range from 40-66 \$/Kg, depending on the size of the tow and the performance requirements. Thus, the CF is very expensive relative to Fiberglass reinforcement, less so relative to the aramid fibers (e.g. Kevlar), and inexpensive with respect to metal or ceramic fibers, such as boron or silicon carbide, which cost about 400-500 \$/Kg.

The estimates of total quantities of carbon fiber (CF) utilized in the U.S.A. for the above applications in 1982 and 1983 are given in Table I. It is seen, first, that the above markets together

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consume nearly as much CF as the aerospace and transportation. Also, contrary to the situation in the seventies, the industrial usage now appears to grow at least as fast as the recreational. The marine applications of CF as far as known, are presently very limited, both in scope and in volume.

Clearly, in order to be utilized, the CF performance has to justify its cost. Summarized in Table II are the CF properties that impart outstanding characteristics to their composites. It should be noted that the first six properties can be measured directly on the CF, while the other four depend not only on the properties of the CF, but also on the matrix material with which the CF is composited, on the fiber orientation in the composite, the strength of fiber -matrix bonding, the stresses in the composite, and the nature of the ambient in which the composite is operated. Most often, it is not a single property that makes the CF composite cost effective, but a combination of two or more of these. For instance, a combination of low density, high stiffness, and good static as well as cyclic stress resistance is necessary in dynamic applications; or high stiffness combined with good electrical conductivity and corrosion resistance is needed in electro-chemical or chemical process applications.

In addition, an increasingly popular approach to the lowering of material costs is to combine some CF with a larger amount of a cheaper reinforcing fiber, especially fiberglass, to generate what is known as hybrid fiber reinforcement. This becomes particularly attractive, if the CF reinforcement is placed at the sites in which the outstanding CF properties are most fully utilized. Such a placement, however, requires familiarity not only with the com-

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ponent material properties, but also the knowledge of the mechanical behavior of such hybrid composites. Obviously, a high degree of design capability and engineering experience is called for.

Also, a CF composite cannot perform adequately unless the fibers are uniformly distributed, properly oriented, and well bonded to the matrix. For CF composites the most common matrix materials are thermosetting resins, such as epoxy-based or polyester-based ones. For use near room temperature the less expensive thermoplastics (e.g. Nylon, polypropylene) may be used. The trend, however, appears to be toward CF composites which can withstand service temperatures over 200°C., and in the recent years polymeric matrix materials, which can be used at 300°C. for up to 1,000 hours, have been developed to meet the ever-increasing aerospace demands. Even though there are hardly any industrial applications requiring service at, say 200°C., at present, there may well be future applications as the use volume increases and the high temperature resin prices drop. Tables III and IV list the most commonly used room temperature and high-temperature, respectively, resins used as matrices in the CF composites. A brief description of the major types of matrix resins can be found in a paper by Judd et al. (1).

Finally, for temperatures over 400°C., inorganic borosilicate glasses, or low melting metal (Al, Mg) alloys, or carbonized polymers or pitches have been developed as matrix materials. As far as known, no significant applications for these materials exist as yet in the industrial sector although many R&D prototypes are being described in the literature.

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INDUSTRIAL APPLICATIONS

STRUCTURES AND PARTS

Moving Parts - In the early seventies much attention was given to the construction of small CF reinforced plastic parts to take advantage of not only the high stiffness/density ratio (* specific stiffness), but also of the better fatigue resistance and vibration damping characteristics in comparison to previously used materials, especially wood. At that time a number of textile machinery parts, like picker sticks, heddle frames, rapier sticks (in shuttle-type weaving looms) or needle bars (in knitting machines) were demonstrated as an advance. Indeed, picker sticks made of Pultruded graphite reportedly allowed a modest, 10%, increase in loom speed and extended the service life from about 6 months to 3 years (2). However, the textile industry has been slow to accept these improvements largely due to the economic conditions not justifying investments in new technology. Other apparently more successful parts made with CF reinforcement have been rolls in paper making and copying machines and carbons in cigarette packaging machines. CF has also been claimed as a reinforcing filler in plastic bushings and bearings providing improved creep and wear resistance (3).

More recently, some moving internal combustion engine parts (e.g. pistons) have been made using CF reinforced high temperature plastics in order to assess the feasibility of a plastic-based, lightweight engine (4). In applications like this, the corrosion and wear resistance of the CF, combined with the strength and stiffness is clearly a cost effective asset. Whether the

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resin matrix is capable of surviving the rigorous ambient remains to be seen. Finally, it is notable that some high speed moving bodies, like rotors, fan blades, flywheels, originally reinforced with CF, are now being built with aramid or fiberglass or hybrid reinforcement as a more cost effective approach.

Stationary Structures 4 Parts - These usually become cost effective by combination of high stiffness (low deflection), a near-zero coefficient of thermal expansion (CTE), and corrosion resistance. The reported applications relate to high quality machine tool supports (5) or instrument parts, such as optical benches, which are usable without the need of precise temparature control, telescope frames, and precision micrometer shafts (6). Other structural items found in the literature are electrical transmissions line tower frames, antenna supports, hollow telephone poles, masts, or booms (7). Other supports used in conjunction with x-ray equipment are mentioned under the Medical Applications.

Structures & Parts for Chemical and Corrosion Resistance - It has been reported that the CF by itself is quite resistant to the chemical attack by strong (50%) hot aqueous acids or alkalis; even more so than the bulk carbons (8). Whenever it is composited, however, it is the resin matrix which is critical to the chemical or corrosion resistance, and different resin systems produce widely different sensitivities to an ambient medium. Data on the chemical resistance of the conventional plastics (epoxies, polyesters, polyolefins, etc.) are readily available, but this is often not the

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case with the newer, high temperature resins polyimides, polyetheretherketones). CF reinforced polyphenylene sulfide (PPS) composite has been molded commercially into valves to be used in piping systems which contain corrosive acids or bases at temperatures in the range of -40 to +150°C. and pressures up to 1.4 MPA (200 psi) (9). Earlier applications have been focused on improving the corrosion resistance of chemical reactors and storage containers by cladding with CF-rich resin linings (10).

Matrix-free "activated" CF has been fabricated by special processes to yield very high absorptive capacities, exceeding in certain cases even those of charcoal. These fibers are being made commercially into aerosol filters to remove air pollutants or toxic contaminants (11, 12).

MEDICAL APPLICATIONS

These applications are promising because of the excellent compatibility of carbon with human tissues in addition to the high CF strength, stiffness and low degree of x-ray absorption of elemental carbon. Since patients can suffer ill effects from large radiation doses, it is a requirement that medical equipment minimize the patient's exposure to x-rays. Any material located between the radiographed patient and the x-ray film will absorb x-rays. The greater the absorption of the material, the greater the x-ray dose that must be used on the patient in order to obtain a satisfactory x-ray picture. The usual items placed between the patient and the film include film casettes and holders and patient supporting structures. In order to yield sharp radiographs, these must exhibit

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minimum deflection under load, yet be as transparent to the x-rays as possible. Both the CF and Kevlar reinforced plastics and their hybrids are well suited for the above structures, such as cantilevered support frames, x-ray table tops, C.A.T. SCAN couches, film holders. These are being produced by a number of manufacturers both in the U.S.A. and abroad.

The high CF stiffness is also useful for artificial limbs. In the U.S.A. the Veterans Administration has funded the development of some prototype components, such as heel and ankle assemblies of an artificial leg, but more remains to be done to make it operational (13). Easier to develop were lightweight external aids such as wheelchairs, braces, and crutches for handicapped and orthopedic patients. For the latter, the fiberglass reinforced plastic casts are often replacing the heavy Plaster of Paris ones, and the use of CF to fashion even lighter but more rigid casts is being mentioned.

Surgical implants containing CF offer a great promise in improving the patient's well-being because of the excellent compatibility between the carbonaceous material and blood or body tissues. CF reinforced carbon pins have been made and used encoessfully for bone adjustments and in heart valves (14). Numerous prosthetic applications such as fixation of artificial limbs to the stumps of the amputated ones, joint replacement by CF/carbon composites (especially hip joint arthroplasty), dental implants, bone plates in osteosynthesis, have been mentioned in both the medical and non-medical literature. Patents claiming CF reinforced body implant compositions exist (15, 16) but it is hard to say whether these applications

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have advanced beyond the research stage.

Finally, filters for improved compatibility with human blood have been developed from bundles of CF, coated with Pyrolytic carbon (17).

ELECTRICAL APPLICATIONS

Continuous CF is nearly as good a conductor as the pitch-bonded bulk-graphite used as the conventional electrode material. Thus, the CF Four is in principle equivalent to a multistrand conductor wire, and CF fabricated into paper or fabric can serve as planar conductors. The cost effectiveness of the electrical uses is based on the combination of electrical conductivity with chemical and wear resistances, favorable electrochemistry or temperature independent conductance.

The earliest application of CF was for heater elements, both as space heaters at low temperatures or as furnace heaters at high temperatures. More recently, CF-containing flexible composite sheet heaters have been introduced (18). Also, the CF is used a filler for structural plastics in order to make them sufficiently conductive to serve as electromagnetic interference (EMI) shielding materials. The advantage of CF is that the quantity of filler needed to achieve a given electrical conductivity level may be up to 100 times lower than the corresponding quantity of a carbon black powder (19). In addition, CF filled plastics may serve as static charge eliminators.

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Process electrodes made of or containing CF have found several applications. The most widely known electrode consists of CF bundles or fabrics arranged in patented configurations (20) and is being used primarily for cathodic reduction of low con centrations of residual metals from spent electrolyte solutions. A wide applicability to various kinds of mining or electroplating industry waste effluents is envisaged. Flexible CF filled sheets have also been proposed as electrodes in such applications (21). The CF in its various forms is also being used as an electrode for the experimental high temperature (325 - 350°C) sodium-sulfur batteries in which the electrode performance usually deteriorates with time (22, 23, In fuel cells felted Cr sheets nave been found useful as the 24). electrode support plates (25). In addition, many other CF containing electrode variants are being researched, especially for small high performance battery applications (26).

Combination of high electroconductivity and low wear rate of the high modulus graphitic fiber can be utilized in sliding current collectors ("brushes"). Both all-fiber brushes (27) as well as brushes fabricated from CF filled metal (Cu, Ag) have been evaluated (28, 29).

The CF has also been used as a means for attaining greatly enhanced electrical conductivities, either by intercalation (30) or by vapor plating with a superconductive compound, such as Nb_3 Sn (31). In the former case the conductivity has been found to approach that of a highly conductive metal, such as copper (32).

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MARINE APPLICATIONS

So far, there are not many marine applications, presumably because of the uncertainty of long term service under a large variety of conditions under water. The Department of Navy is sponsoring the development of two experimental grap. ite-epoxy structural elements patterned after real components of a hydrofoil patrol boat -- a section of a box beam, ca. 1.2 m long, and a hydrofoil control flap (2m x 0.5 m in size). These parts are presently undergoing a variety of simulated service tests (33). In the commercial sector some racing canoes and kayaks are being stiffened longitudinally with a layup of CF/epoxy tapes, in the otherwise fiberglass-polyester body in order to improve their competitive performance. Lately, however, the CF is being replaced by the less costly aramid, and this trend may continue as long as the part does not have to bear sizable compressive or shear loads.

RECREATIONAL APPLICATIONS

<u>Sports Equipment</u> - Here is a very interesting situation where the products are not cost sensitive, but are purchased either for prestige or improvements which matter only to the pros and semipros of that sport. Several of these are large volume applications, even though the amount of CF in each item may be relatively small, typically 0.1 Kg. or less. The first of these products was the golf club with a "graphite" fiber containing shaft. The high specific softness of a properly designed shaft resulted in a lighter shaft, allowing to put more weight in the club head and thus attain a longer driving distance owing to the enhanced momentum transfer from the heavier head to the ball. The consumption of CF for golf

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shafts made a spectacular jump from maybe a few hundred Kg in 1972 to ca. 20,000 Kg in 1973 continuing roughly at that level until 1979. Then it resumed growth, because the cost savings resulting from more efficient prepregging and club assembly processes, increased the sales all over the world. Presently, the consumption of U.S. CF in the golf shafts is estimated at ca. 35,000 Kg./year.

A few years later a similar boom started in fishing rods and tennis recquets. The demand for the former grew at the fastest rate because these CF-epoxy rods are substantially lighter than those made of other materials and owing to the inherent CF stiffness will give an improved casting accuracy and better control of the lure. Presently most of the recreational CF goes into fishing rods, with tennis rackets running a close second, and golf shafts in third place.

Other sports equipment items in limited production are selectively reinforced surfboards, hockey stick blades, bows, oars and paddles, arrow shafts, bicycle frames, molded racquets for ball or squash games. A discussion of the dominant patents pertaining to their manufacture is given in reference (7). A survey of the history and con sumption of the CF for the sporting products was published recently (34). The total present consumption of CF in sporting goods is now estimated at about 130,000 Kg/year.

Other Sports

There are a few speciality sports areas that incorporate advanced design features and use CF-epoxy composites. Che such is the competitive racing car in which the CF-epoxy composte is used to lower the chasis weight while maintaining strength and stiffness.

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to lower the chasis' weight while maintaining strength and stiffness. Presently, the most successful is the McLaren Formula I racing car which won both Grand Prix races in the U.S. in the summer of 1982 (35). A newly designed two-seat racing car with CF-epoxy chassis, called Mustang GTP, was disclosed by the Ford Motor Co. in May, 1983 (4).

LOUDSPEAKERS & MUSICAL INSTRUMENTS

High modulus carbon fibers are also being used to make high quality loudspeakers, because the speed of sound on the surface of a molded CF-filled plastic speaker cone is several times that on the surface of a regular speaker, allowing the use of a shallower cone which is either less conspicuous or can be fitted into otherwise inaccessible areas. These speakers are made in Japan and are being continually improved (36). Violins and guitars have been designed and built employing CF-epoxy soundboards that are claimed to be more reliable than those of word, stay tuned, and offer improved sound radiation qualities over those of wood. A number of such soundboards or assemblies are covered by patents (37 - 39). One of these patented guitarr was reported to sell for \$2,500; which would seem to keep it away from the fingers of most amateur guitarists.

SUMMARY

It is seen that the CF applications are extremely diverse and may not involve cost effectiveness, especially in the areas of competitive sports. Nevertheless, the CF containing materials will alleviate some world wide problems by providing 1) energy savings through the use of light weight parts, 2) material savings

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resulting from extended service life due to reduced chemical attack and corrosion, and 3) improved quality of life by means of long lasting biocompatible body parts and accessories and by decreasing the environmental contamination due to certain toxic wastes.

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TABLE 1

ESTIMATED CARBON FIBER USAGE FOR 1982 & 1983 (1)

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	1983 Amount			1982 Amount		
Market Sector	10 ⁶ lbs.	Metric Tons	•	10 ⁶ 1bs.	Metric Tons	1
Aircraft, Space Vehicles	1.30	585	50	1.0	455	49
Industrial, Marine, Miscellaneous	0.63	285	24	0.47	215	23
Sports, Recreation	0.52	235	20	0.45	205	22
Sample handouts, Fabrication losses	0.15	65	6	0.13	60	6
TOTAL	2.6	1170	100	2.05	935	100

(1) Adapted from the market surveys by Composite Market Reports, Inc., San Diego, Calif.

TABLE II

OUTSTANDING CARBON FIBER AND THEIR COMPOSITE PROPERTIES

Property Typical Values or Comment o Low density $1.7 - 2.0 \text{ Kg} / \text{dm}^3$ o High tensile stiffness (modulus) 200 - 400 x 10⁹ Pa (GPA) $2.5 - 3.5 \text{ GPA} (10^9 \text{ Pa})$ o High tensile strength o Very small axial thermal $-2 \times 10^{-7} \text{ K}^{-1}$ expansion coefficient $5 - 20 \times 10^4$ ohm⁻¹ m⁻¹ (in comparison o High electrical conductivity to non-metals $6 - 140 \text{ W}.\overline{m}^{1} \text{ K}^{-1}$ or semi-conductors, o High thermal conductivity Long service life at relatively Commonly know high constant or cyclic strain resistances" Commonly known as "creep and fatigue and stresses o Corrosion resistance CF is attacked only by strong oxidizers at elevated temperatures. o Biocompatibility Particularly for the higher modulus CF o Low friction coefficient and

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good wear resistance.

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TABLE III

COMMONLY USED ROOM TEMPERATURE MATRIX RESINS

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Name of Resin	Composition
Epoxide, epoxy	di - tri - or tetra-glycidyl¢thers of various substituted phenols or polyphenols.
Polyester (unsaturated)	Condensates of dialcohols with un- saturated dibasic carboxylic acids or anhydrides plus cross-linkable vinyl monomers.
Phenolic	Condensates of polymerized phenol- formaldehyde.
Polyolefin	Polymerized ethylene or propylene.
Polyester (saturated)	Condensates of dialcohols with various, mostly saturated dibasic carboxylic acids or anhydrides

TABLE IV

HIGH TEMPERATURE MATRIX RESINS

Polymer Type	Designation or Trade Name	Initial Polymerizable Components
Amide-imide copolymer	Torlon	Trimellitic anhydride; aromatic diamines
Polyimide	PMR-15	Esters of benzophenone tetra- carboxylic acid (BTDE) and of norbornene dicarboxylic acid (NE); aromatic diamines.
•	LARC-160	Esters of BTDE and NE; aromatic polyamines.
•	Thermid 600	Benzophenone tetracarboxylic dianhydride; bis (3-aminophenoxy) benzene; metaaminophenylacetylene
Polyetherether Ketone	PEEK	Dihydroquinone; dichlorobenzo- phenone

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