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Mechanical Properties and Applications of Pitch-Based Carbon Fiber Reinforced Plastics (CFRP)

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Abstract:

The high-performance pitch-based carbon fibers developed by Nippon Steel Corporation make ingenious use of mesophase prepared from highly refined pitch (optically anisotropic pitch), and feature high strength and high elastic modulus of 50 through 80 tf/mm^2. This paper describes the properties of these fibers, the optimum design of composite materials to take advantage of the fiber properties, and composite products reinforced by the fibers.

1. Introduction

There are various types of carbon fibers. They are broadly classified by the type of fiber precursor into pitch-based, polyacrylonitrile (PAN)-based, rayon-based, and vapor growth fiber-based carbon fibers. With regards the pitch-based carbon fibers, general-purpose carbon fibers are produced from optically isotropic pitch, while high-performance carbon fibers are prepared from optically anisotropic (mesophase) pitch[1,2]. These types of carbon fibers have basically different properties. It is therefore essential that the properties of specific carbon fibers be best utilized in developing their applications.

PAN-based carbon fibers were industrially produced on the basis of the invention by Shindo[3], commercially applied to fishing rods for the first time in the early years of the 1970s, and then to golf club shafts and tennis rackets, followed by such principal structural members as in military aircraft and large passenger airplanes. As central components of advanced composite materials (ACMs), PAN-based carbon fibers have made great contribution to weight reduction and functional enhancement in structural and functional materials. With such diversification of demand, the annual world production of PAN-based carbon fibers, which marked only five tons about 20 years ago, increased to above 1,000 tons 10 years later, and the demand now stands at 7,000 tons/year.

The basic technology of high-performance pitch-based carbon fibers originates in the research by Otani[4,5]. Subsequently on the basis of the technology developed by Singer[6], Union Carbide Corporation of the United States commercialized it for the first time in the world. Later, Amoco Performance Products of the United States tookover the business of carbon fibers from Union Carbide.

This article describes the properties of composite materials using pitch-based carbon fibers and introduces composite products that make efficient use of the high strength and high elastic modulus of pitch-based carbon fibers.

2. Mechanical Properties of High Elastic Modulus Pitch-Based Carbon Fiber Reinforced Composites

High-performance pitch-based carbon fibers are a new material technology that is still in the stage of developing. Being carbon fibers, they share some of the fiber properties, applications, and technologies with the PAN-based carbon fibers. In many other points, however, the pitch-based carbon fibers considerably differ from the PAN-based ones and cannot be equated with the latter[7,8].

Aside from mechanical properties, the pitch-based carbon fibers possess many interesting properties such as density, thermal and electromagnetic properties, oxidation resistance, and chemical properties. Because of these peculiar properties, they often exhibit advantageous behaviors over the PAN-based carbon fibers. On the strength of these properties, they are expected to find applications as functional and structural materials in various fields.

Carbon fibers, on the other hand, are widely used in the field of structural members. Making the most of their light weight, high elastic modulus and high strength, carbon fibers are used in a polymer-matrix composite called carbon fiber reinforced plas-

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tics (CFRP). Using high elastic modulus fibers as structural members, however, calls for the development of application technology so that their meritorious properties can be best exploited. Generally speaking, carbon fibers decrease in tensile failure elongation to become more brittle and difficult to handle proportionately with increasing elastic modulus. Strength and elastic modulus widely vary with fiber grade, and properties along the fiber axis (0° direction) are substantially different from those across the fiber axis (90° direction). Discussed hereunder are the tensile, compressive, and fatigue properties of high elastic modulus pitch-based carbon fiber reinforced composites in their application as structural materials.

2.1 Stress-strain characteristics in fiber direction of unidirectional CFRP

Fig. 1 shows the typical tensile and compressive stress-strain curves of unidirectional CFRP fabricated from pitch-based carbon fibers. The stress-strain relationship is nonlinear, and no permanent deformation is left. A feature of composite materials reinforced by high elastic modulus carbon fibers is that compressive strength is generally lower than tensile strength in the fiber direction. This fact must be taken into account when using such composite materials. Characteristics of unidirectional CFRP may be summarized as follows[9,10]:

(1) Tensile elastic modulus in the fiber direction increases with increasing tensile strain.
(2) Compressive elastic modulus in the fiber direction sharply decreases with increasing compressive strain.
(3) When unloading, both of them trace back the boading path, and recover without leaving any permanent deformation when the stress has been completely removed.

2.1.1 Tensile properties

Tensile elastic modulus E of carbon fibers is given as a function of tensile strain ε by:

$$E = E_0 (1 + a \cdot \varepsilon)$$

where E_0 is elastic modulus (initial elastic modulus) in the fiber direction when the strain is zero, and a is a constant characteristic of a given carbon fiber and indicates a degree of nonlinearity. The strain dependence of tensile elastic modulus can be explained by assuming that pulling the carbon fiber in the fiber direction rotates graphite crystallites toward the fiber direction. As the elastic modulus of the carbon fiber increases, graphite crystallites grow and at the same time are aligned (oriented) parallel to the fiber direction. Therefore, when the elastic modulus becomes higher, the rotation of graphite crystallites toward the fiber axis due to tensile strain along the fiber axis decreases, resulting in decreasing the degree of nonlinearity. This also agrees with the fact that the constant a decreases with increasing tensile modulus. Since the rotation of graphite crystallites occurs reversibly, the tensile stress-strain relationship is reversible.

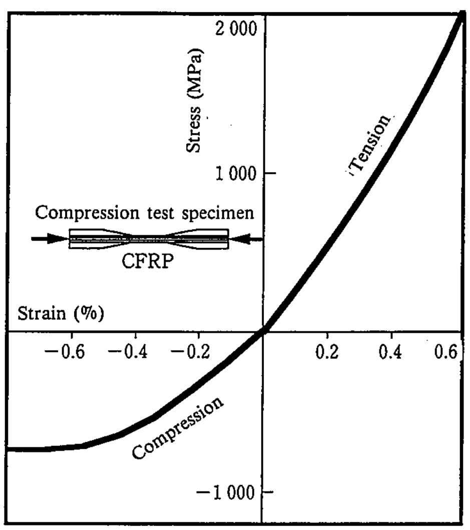


Fig. 1 Longitudinal stress-strain curves of unidirectional CFRP

2.1.2 Compressive properties

Unidirectional CFRP produced from high elastic modulus pitch-based carbon fibers becomes nonlinear with a small amount of strain when stressed in compression, and leaves no permanent deformation, which deffers from the plastic deformation of metals. This property is peculiar to this material. Attempts were made to find the cause of this property apart from fiber properties, in the nonlinearity of the resin matrix, misorientation of the fibers, interface between the resin matrix and fibers, or local buckling in composite materials, but to no avail. When the resin is compressed or when the fibers are misaligned the unidirectional CFRP exhibits nonlinearity (or gradually decreases in elastic modulus). The amount of strain in this case is far larger than anticipated, and, further, it should leave permanent strain when unloaded. This is true also of interfacial slip and local buckling, and therefore the reversibility and small amount of strain make it difficult to explain this nonlinearity property of the unidirectional CFRP.

The carbon fibers are fine and measure only 6 to 10 μm in diameter, so that their compressive stress-strain relationship is difficult to measure. Their compressive strength, however, can be measured, although indirectly, by such methods as the fiber fragmentation, piezo-resistance, loop, and tensile recoil methods. And, the compressive strength of high elastic modulus pitch-based carbon fibers cannot be explained but by assuming a nonlinear stress-strain relationship. The recoil test results, in particular, can be quantitatively explained if the nonlinearity of unidirectional CFRP is assumed to be derived from carbon fibers[11].

Considering that the nonlinearity of unidirectional CFRP originates in the carbon fibers as discussed above, the authors[9,10] proposed a nonlinear sublayer model as illustrated in **Fig. 2**. First, the carbon fiber is assumed to be composed of several sublayers as shown in **Fig. 2(a)**. The load-strain relationship of each sublayer is as represented in Fig. 2(b). This relationship is the same as for a perfect elastic-plastic material, but is considered to trace the loading path when unloaded. In other words, the load-axial deflection relationship of an Euler buckled column is assumed. Then the load-axial deflection relationship becomes nonlinear as shown in **Fig. 2(c)** and reversible when the carbon fiber is loaded and unloaded. Such stress-strain relationship actually applies to only one portion of each sublayer, and stress transfer is considered to occur as shown in **Fig. 2(d)** when a given portion of the carbon fiber loses its tangent modulus.

Fig. 3 shows the effect of compressive strain on the ratio of tangential modulus E_t to the initial modulus E_0 of unidirectional CFRP. In the figure, A, B, C, and D are materials which use pitch-based carbon fibers with tensile modulus of 20, 40, 50, and 60 tf/mm^2, respectively. From the figure, it is evident that the

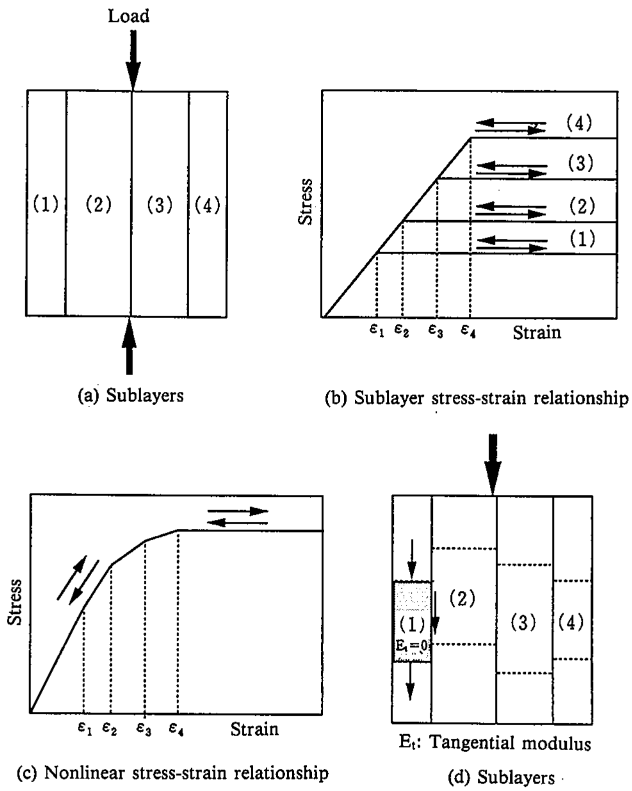


Fig. 2 Sublayer model to explain nonlinearity of carbon fibers under compression

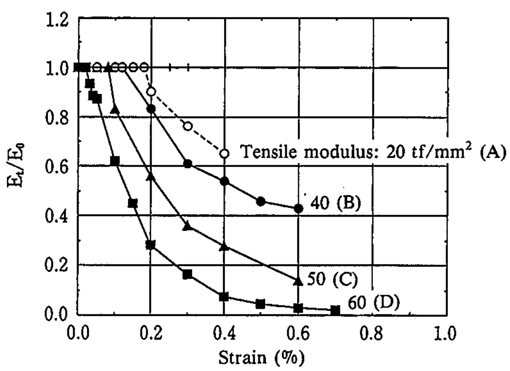


Fig. 3 Change in compressive modulus with compressive strain

proportion of compressive nonlinearity degree increases with increasing tensile modulus of the carbon fibers. The compressive strength decreases accordingly as already described.

As the pitch-based carbon fibers increase in the tensile modulus, fine graphite crystallites grow in size and are well oriented in the fiber direction. Increasing the elastic modulus is therefore considered to increase the length of each sublayer. As a result, a small load causes the carbon fiber to buckle (decrease in compressive strength), and a small strain causes the carbon fiber to lose its elastic modulus. Thus, the increase of nonlinearity and decrease of compressive strength can both be explained. The correlation between carbon fiber elements equivalent to the sublayers and the internal structure of the carbon fiber (for example, graphite crystals) is still to be clarified through continued study.

Photo 1 shows kink bands observed on the compression side of monofilaments when looped[12]. The carbon fibers do not fracture even when the compressive strain is more than 10 times the compressive fracture strain obtained in the compression testing of composite materials. It is presumed that buckling is caused in same way in the carbon fibers by the formation of kink bands. The filaments that revealed the kink bands were tension tested, but exhibited no decrease in the tensile strength.

2.2 Transverse properties

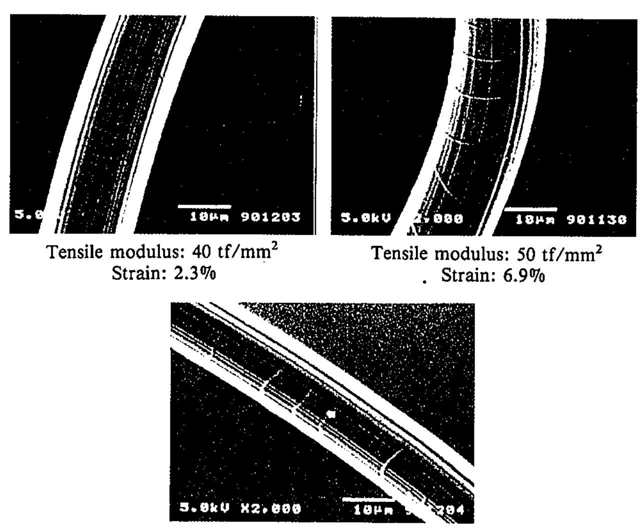
The elastic modulus and strength of unidirectional CFRP in the transverse direction (normal to the fiber direction) are substantially smaller than in the tensile direction. The matrix resin and carbon fibers can be assumed to be aligned in series when considering transverse, not linear, stress transfer. Even from this assumption, it is obvious that the strength and elastic modulus of unidirectional CFRP in the transverse direction are far smaller than in the fiber direction. Furthermore, the high elastic modulus pitch-based carbon fibers have graphite crystals oriented along the fiber direction and weakly bonded to each other, so that they are easily fractured as if in fiber tearing. Special care must therefore be exercised in selecting bond strength between the resin and carbon fiber[13].

2.3 Fatigue properties

The fatigue strength of CFRP is generally said to be higher than that of metals, but there have been few researches carried out on the fatigue properties of CFRP reinforced with high elastic modulus pitch-based carbon fibers. To clarify the effect of nonlinearity on fatigue strength, the authors devised a method for testing fatigue strength under compressive and tensile stresses, and evaluated the fatigue properties of unidirectional CFRP[14,15]. The test results are shown in **Fig. 4**. It was confirmed that the fatigue strength of unidirectional CFRP is not substantially lowered by compressive stress and that nonlinearity has no or little influence on the fatigue strength of unidirectional CFRP.

2.4 Bolted joint strength

Composites are rarely used singly but are often used in com-



Tensile modulus: 40 tf/mm² Strain: 2.3%

Tensile modulus: 50 tf/mm² Strain: 6.9%

Tensile modulus: 60 tf/mm² Strain: 2.2%

Photo 1 Kink bands in carbon fibers

bination with other composites and metals. The joint strength of high elastic modulus carbon fiber-reinforced composites has been scarcely researched on. The authors investigated the effect of carbon fiber properties on the bolt hole bearing strength of composites[16,17] and found that it was governed by the compressive strength in the fiber direction. The authors also elucidated the fracture mechanism involved as well as the relationship between the bolt hole center position from the bolted joint edge and the bolt hole diameter. **Fig. 5** shows the relationship between the compressive strength and bolt hole bearing strength of unidirectional CFRP.

2.5 Improvement in compressive strength by hybrid method

The longitudinal compressive properties of unidirectional carbon fiber-reinforced composites are evaluated in many cases by the Celanese method specified in ASTM D 3410-75 (the specimen shape is as shown in **Fig. 1**). When unidirectional CFRP prepared from high elastic modulus pitch-based carbon fibers is compression tested, the specimen buckles under shear stress because of decreased elastic modulus and shear modulus. Since this results in a shear fracture, the compressive fracture strain inherently possessed by carbon fibers is not likely to present itself in this case. **Photo 2** shows the compressive fracture surface of the specimen. As already described, the fracture strain of carbon fibers themselves is considered to be far greater than the one measured by the Celanese method.

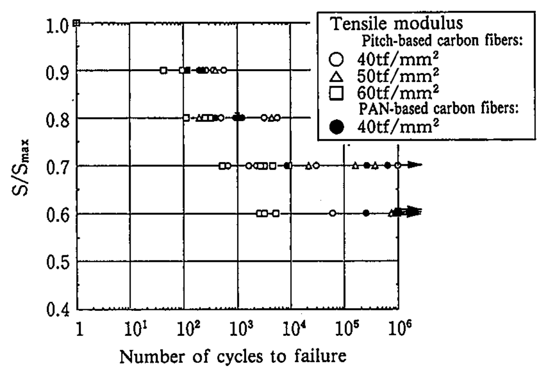


Fig. 4 Fatigue properties of high elastic modulus CFRP under completely reversed three-point bending (stress ratio R = −1.0). Stress amplitude is divided by static strength and made dimensionless.

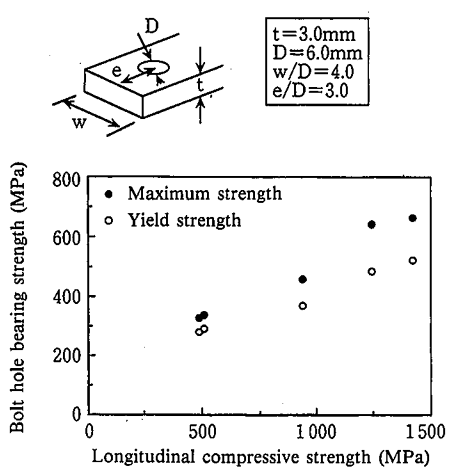


Fig. 5 Bolt hole bearing strength versus longitudinal compressive strength of CFRP

In the case of tensile test, the specimen fracture occurs when the tensile strain reaches the tensile fracture strain of the carbon fiber. When two fibers having different fracture strengths are mixed (hybridized) and used to make a specimen, the specimen is fractured by tension when the tensile strain reaches the smaller fracture strain value of either fiber. The strength of the specimen is thus smaller than the weighted sum of the strengths of the two fibers. The authors found, however, that this phenomenon is somewhat different in the case of the compression of high elastic modulus pitch-based carbon fibers.

Fig. 6 shows the stress-strain curves by the Celanese method of compression specimens prepared by the hybridization in different proportions of fiber A having large nonlinearity and low compressive strength and with fiber B having practically no nonlinearity and high compressive strength. In the figure, curve C_1 is for specimens made of the fiber A alone, curves C_2, C_3 and C_4 are for specimens with increasing proportions of fiber B in that order, and curve C_5 is for specimens made of fiber B alone. Although the initial compressive elastic modulus of fiber A specimens is higher than that of fiber B specimens, the decrease of compressive elastic modulus is much greater for fiber A speci-

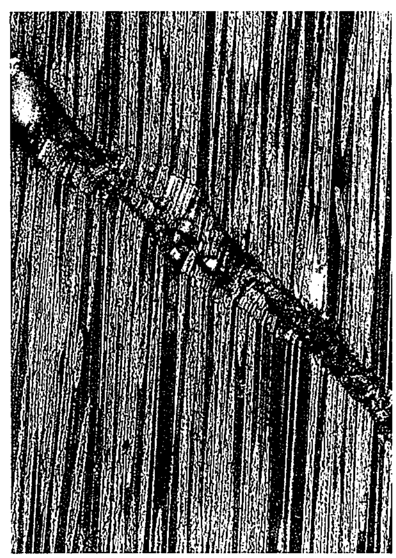


Photo 2 Compressive fracture surface of CFRP

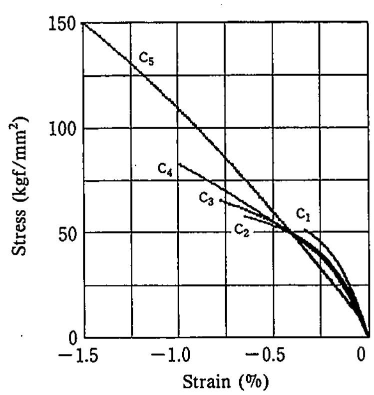


Fig. 6 Compressive stress-strain curves of composites reinforced by mixing and hybridization of carbon fiber A with low compressive strength and large nonlinearity and of carbon fiber B with low compressive elastic modulus and small nonlinearity

mens than for fiber B specimens. Furthermore, the compressive strength (fracture stress) and fracture strain of fiber A specimens are smaller than those of fiber B specimens. As clear from **Fig. 6**, both the fracture strain and fracture strength improves with increasing proportion of fiber B. Not as in the above-mentioned tension testing, the fracture strain of fiber A does not govern that of the entire specimen.

Not shown in **Fig. 6**, though, it is confirmed that the compressive stress path when unloading traces back the curves shown in the figure. When specimens C_2 through C_4 were precisely observed at a point over the maximum compressive strain value of curve C_1, no fracture was observed in the specimen portions corresponding to fiber A. This phenomenon points to the prevention of microbuckling by the presence of fiber B. As a result, the inherently large fracture strain of fiber A is presumably brought to work to increase the fracture strain of the specimen.

In practical application of this principle, Nippon Steel developed hybrid prepregs[18] with improved compressive strength and compressive fracture strain, and placed them on the market.

3. Development of New Applications to Best Exploit High Elastic Modulus Properties

The preceding section described that the pitch-based carbon fiber reinforced composites are nonlinear in the fiber direction and posses particularly large nonlinearity for compression[9,10], and that high elastic modulus carbon fibers have low compressive strength regardless of whether they are pitch-based or PAN-based. These facts must be taken into account when composites reinforced by high elastic modulus pitch-based carbon fibers are used as structural materials. Applications in which these properties of CFRP can be put to effective use in structural members may be summarized as follows:

(1) High flexural rigidity is required, but not high flexural strength in particular.
(2) High tensile modulus and high tensile strength are required.
(3) High tensile strength and high compressive fracture strain are required.
(4) High tensile modulus and high thermal conductivity are required.
(5) High torsional rigidity is required, but high torsional strength is not required.

Application technology is under development particularly for (1) through (3) mentioned above. In the case of (4), CFRP is utilized as members for satellites. Application of high torsional rigidity in (5) is now being searched for and is expected to be found soon.

3.1 CFRP rolls

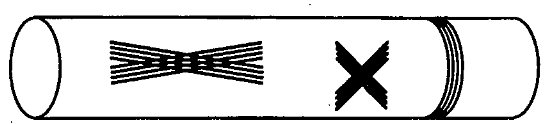
CFRP rolls are a typical case in which high flexural rigidity can be put to effective use. Many metal rolls are used on plastic film and paper production lines, but are being replaced by CFRP rolls. For the manufacture of high-performance roll products, it is indispensable to reduce the rotational inertia and bending deflection of rolls. CFRP serves this purpose well because its specific gravity is one-fifth of that of iron and its elastic modulus is high. As shown in **Fig. 7**, fibers oriented in the axial direction at an angle of 45° and at 90° to the axial direction contribute to the flexural rigidity, torsional rigidity, and flattening rigidity of the pipe, respectively. In this way, CFRP pipes with various properties can be designed by judiciously selecting the orientation, amount, and elastic modulus of the fiber. Pipe flexural rigidity equal or superior to that of steel can also be obtained.

As described above, CFRP has high specific modulus and high damping capacity, and thus is an ideal material for rolls. Large CFRP rolls, however, had problems with as-formed pipe roundness, metal journal joint and durability, and therefore had not been commercialized until Nippon Steel developed large and long CFRP rolls with light weight, high flexural rigidity and small runout. This was accomplished through the establishment of proper forming and designing technologies. That is, a long CFRP pipe was formed by the filament winding process in which the shape of the accurate outside diameter of a mandrel was transferred to the inside diameter of the CFRP pipe, and inside diameter tolerances that would not be obtainable from metal machining were accomplished. Further, the high finishing accuracy and high specific modulus helped to produce long CFRP rolls with small runout at high speed and notably small deflection under gravity. These rolls, developed as plastic film rewinder sensor rolls and dancer rolls, measured 7.8 m long and 48 cm outside diameter, and weighed 430 kg, which is shown in **Photo 3**[19,20].

The CFRP roll technology mentioned above demonstrated Nippon Steel's technical levels at several exhibitions, including the first Japan SAMPE symposium and the exhibition in the Makuhari Messe, Chiba Prefecture held in 1989. In May 1992, it was awarded a technology prize by the Japan Society for Composite Materials for its great contribution to the improvement and expansion of carbon fiber utilization technology.

3.2 Ultrahigh-speed rotating drums

When CFRP is studied for use in ultrahigh-speed rotating machines, it should be noted that the specific strength of the material is a governing factor in designing a rotating drum if it is entirely made up of CFRP. It is therefore natural that high-strength carbon fibers should be used. A metal pipe, however, is often used inside the rotating drum of many ultrahigh-speed



±45°: Torsional rigidity
±15°: Flexural rigidity
90°: Flattening rigidity

Fig. 7 CFRP pipe forming procedure. Angles indicate fiber direction with respect to pipe axial direction.

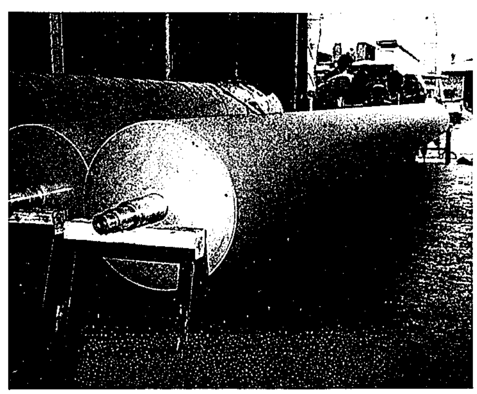


Photo 3 Long CFRP rolls

rotating machines. In this case, since the elongation, i.e., the strength of the metal, becomes a governing factor, the deflection of the metal must be controlled to increase the speed of the rotating drum. Wrapping the metal with high elastic modulus pitch-based carbon fiber helps to restrain its deflection in order to raise the velocity of drum revolution. In this type of carbon fiber application, the compressive strength is not an issue, but tensile strength and modulus need be considered.

3.3 Tensile members

Pitch-based carbon fibers have relatively low compressive strength in the high elastic modulus region, but possess rather high compressive fracture strain, compared with that of the PAN-based one. These properties can be effectively utilized by a method in which structural members are designed to carry tensile loads and avoid, compressive loads due to buckling. This method is employed for braces of many truss structures, and Nippon Steel has developed its original method for application to large structures.

3.4 Other applications

We have discussed about the methods of best utilizing the peculiar strength and modulus of high elastic modulus pitch-based carbon fiber reinforced composites. Among other applications are: golf club shafts, fishing rods and drive shafts where light weight and high elastic modulus are utilized; medical equipment where high X-ray transparency is utilized; artificial satellite panels and frames where high elastic modulus and high thermal conductivity are utilized; and superconducting structures where non-magnetic properties are utilized.

A monocoque bicycle frame[21,22] (see **Photo 4**) developed by Nippon Steel uses high elastic modulus pitch-based carbon fibers to provide light weight and high rigidity which are not obtainable merely from high-strength fiber-reinforced composite materials. The structural design, odd-shaped hollow pipe forming, and assembly techniques acquired through the development project, established a basis for the subsequent development of composite fabrication technology by the Nippon Steel group. The monocoque bicycle frame technology was honored with a 1990 award by the Japan Reinforced Plastics Society. Furthermore, the cables reinforced by carbon fibers shown in **Photo 5** are much more lightweight than conventional steel cables. They are now extensively used as materials for the construction of underground structures and bridges. These applications best utilize the high tensile modulus and strength of high-performance pitch-based carbon fibers.

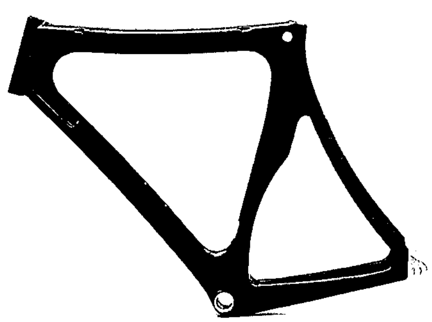


Photo 4 CFRP monocoque bicycle frame

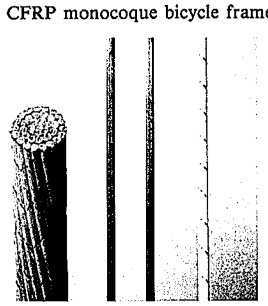


Photo 5 CFRP cables

4. Conclusions

With the progress of high elastic modulus pitch-based carbon fiber manufacturing technology, Nippon Steel has carried out research and development work on the technologies of evaluating and utilizing composites reinforced by high elastic modulus pitch-based carbon fibers. Remarkable progress has been made in the discovery of the peculiar properties of composites, clarification of mechanisms whereby such outstanding properties are developed, and the development of technology to effectively utilize these properties. The composites, however, have not yet been fully accepted in the market, and the situation calls for a further progress in the application technology. Continued technology development efforts will be essential for them to firmly establish their position in the advanced material market.

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