Technology

Properties and Applications of Pitch-based Carbon Fiber GRANOC™

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Abstract

Pitch-based carbon fibers have excellent mechanical and thermal properties, which can be controlled by adjusting the properties of the pitch raw materials and the manufacturing conditions of its precursors. In recent years, it has become an indispensable material for the design of advanced components in the industrial, sports and leisure, satellite, and thermal management fields. Nippon Graphite Fiber Corporation is the only company that provides pitch-based continuous carbon fiber GRANOC™ from ultra-low modulus grades with a tensile modulus of 55 GPa to ultra-high modulus grades up to 920 GPa. This paper introduces the properties and applications of GRANOC™.

1. Introduction

Carbonizing coal in coke ovens produces coal tar containing pitch in the process. Pitch is used as a raw material for special carbon materials, including artificial graphite electrodes, in wide-ranging fields. Nippon Graphite Fiber Corporation (NGF) manufactures carbon fibers from impregnated pitch, which is used as an impregnation material when artificial graphite electrodes are manufactured, and sells them. Carbon fibers are defined as fibers that are obtained by heating and carbonizing organic fibers and for which the carbon content is 90% or higher.[1] Carbon fibers are broadly divided into two types according to the raw material type: PAN-based carbon fibers that are produced from polyacrylonitrile (PAN), which is an acrylic resin, and pitch-based carbon fibers that are manufactured from coal tar pitch and petroleum pitch. PAN-based carbon fibers are mostly in demand among carbon fibers. PAN-based carbon fibers have been increasingly adopted for applications for aircraft, wind turbine blades, and automobiles because of the promotion of carbon neutrality and rising environmental awareness around the world and the demand has been increasing year after year. Under such circumstances, new manufacturers –mainly Chinese manufacturers– have started to join the market and existing manufacturers have started investing in production facilities one after another. The annual production has reached as high as 250 000 to 300 000 tons (including large- and regular-tow). Meanwhile, continuous pitch-based carbon fibers are supplied to the market by three manufacturers (two in Japan and one in the U.S.), including Nippon Graphite Fiber. The total annual production capacity of the three companies is approximately 1 400 tons. Although the market of pitch-based carbon fibers is much smaller than that of PAN-based fibers, pitch-based carbon fibers are indispensable to the design of advanced components in the industrial, sports and leisure, and satellite fields. This paper introduces the applications that fully utilize the properties of pitch-based carbon fibers and adopted cases.

2. Advantages of Pitch-based Carbon Fibers

Figure 1 shows the correlation between the tensile modulus and the tensile strength of various carbon fibers. Nippon Graphite Fiber manufactures, by adjusting the conditions for modifying impregnated pitch and for spinning and heating precursors, pitch-based carbon fiber products in two grades: Low modulus grade (54 to 155 GPa) and high modulus grade (520 GPa or higher). This grading differentiates the market of our original products from that of PAN-based fibers for which the main moduli are 230 to 300 GPa and we found out our original product value. Compared with PAN-based fibers, pitch-based fibers are more cost effective when fibers with elastic moduli of 520 GPa or higher are manufactured because their aromatic rings are fully grown and more highly oriented, particularly at the precursor stage.

To manufacture products with various elastic moduli, it is necessary, as the first step, to modify impregnated pitch to a pitch raw material for spinning that matches the production of each grade. The properties of a pitch raw material for spinning greatly affect the fine

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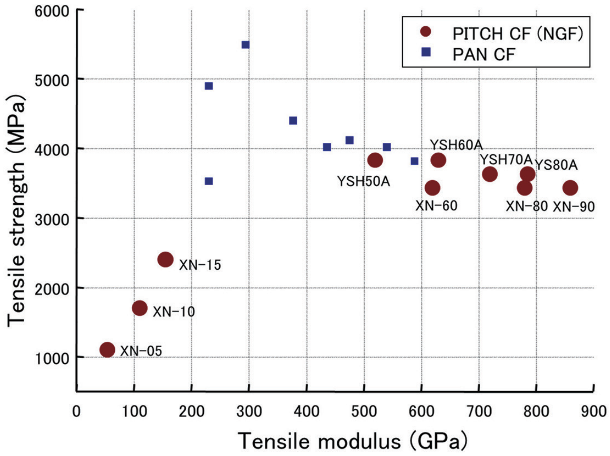

Fig. 1 **Mechanical properties of carbon fibers (Tensile strength and modulus)**

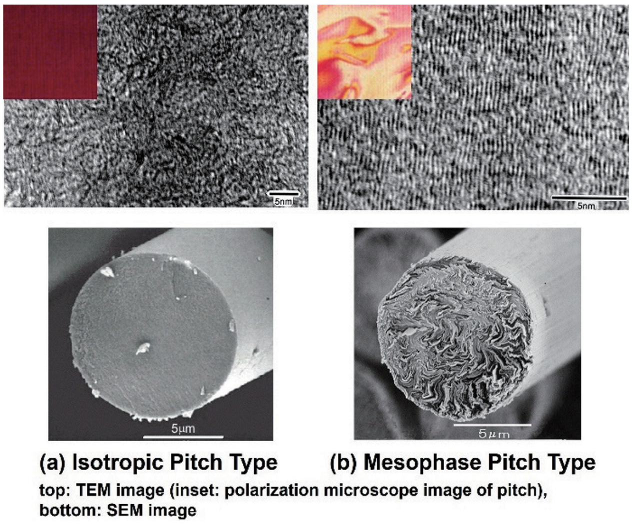

Fig. 2 **TEM and SEM images of pitch-based carbon fiber**

structure and physical properties of ultimate carbon fibers. Pitch can be divided into two types: Isotropic pitch that is optically disordered and that shows no polarization and anisotropic pitch (mesophase pitch) that has a property like liquid crystals where the regularity of the molecular arrangement is retained even in a molten state. When precursors using isotropic pitch, which is for some low modulus grades, is heat-treated at high temperatures, graphite crystals do not grow much and the uniform amorphous carbon structure is obtained. Therefore, the carbon fibers obtained are lightweight and flexible. On the other hand, when precursors using mesophase pitch are heat-treated at high temperatures of 2000°C or higher, graphite crystals grow. **Figure 2** shows the SEM images of the transverse sections of carbon fibers and the TEM images of the longitudinal sections.[2] For the carbon fiber for which mesophase pitch was used as the raw material, graphitic planes are observed on the transverse section and graphite crystals have formed orderly lines in the fiber axis direction. This orderly arrangement of graphite crystals is the origin of the excellent properties of high modulus carbon fibers, such as high rigidity, excellent vibration damping property, and high thermal conductivity.

Carbon fibers having these characteristics are mainly combined with matrix resin (e.g., epoxy resin) to produce a composite material (carbon fiber reinforced plastics (CFRP)). The types of carbon fibers and resin are selected according to the application, and this varies the mechanical properties of CFRP, which cannot be achieved by carbon fibers or resin alone. In recent years, in addition to thermosetting resin (having a hardening property due to heating) represented by epoxy resin, thermoplastic resin (having a softening property due to heating) has also been increasingly adopted to reduce the molding time during composite material production and enhance the recycling efficiency.

3. Product Forms of Pitch-based Carbon Fiber GRANOC™ and its Applications

Nippon Graphite Fiber is the only manufacturer in the world to put both low modulus carbon fibers (elastic moduli of 54 to 155 GPa) and high modulus carbon fibers (elastic moduli of 520 to 920 GPa) onto the market. The company provides its product GRANOC™[*1] in the forms of yarn (continuous fiber), chopped/milled fiber, dry fabric, and prepreg (sheet impregnated with thermosetting resin) (**Table 1**).

3.1 Low modulus grade

Nippon Graphite Fiber supplies low modulus carbon fibers with elastic moduli of 155 GPa or lower, including ultralow modulus amorphous carbon fibers (XN-05), in the forms of yarn and prepreg. Except for Nippon Graphite Fiber, there are no other manufacturers in the world that provide such products. **Table 2** lists the physical properties of low modulus carbon fibers, other reinforced fibers, and their composites.[3] Low modulus carbon fibers with a density of 1.65 to 1.85 are a material that is lighter than glass fibers by approximately 30%. In addition, the tensile/compressive elastic moduli of their composites are 30 to 90 GPa, so there are wide-ranging alternatives and they are appropriate for adjusting the flexibility of components requiring low elasticity. The compressive strength values of the composites involving low modulus carbon fiber GRANOC™ are higher than those of the glass and aramid fibers. In the fiber structure of aramid fibers (organic fibers), etc., chain-like structures spreading in the fiber axis direction have gathered due to aggregation between the molecules, so their compressive strength is remarkably low. Compared with PAN-based carbon fibers and other reinforced fiber materials, the failure strain of low modulus carbon fiber GRANOC™ against compression is higher and the balance between the tensile strength and the compressive strength is better. Accordingly, when laminate design where strength and flexibility are important is considered, arranging GRANOC™ in the external layer section on the compressive load side of a component on which bending fracture occurs works as reinforcement against loads, which can enhance the bending strength of the entire component.

Using these characteristics, GRANOC™ low modulus carbon fibers have been increasingly adopted for golf club shafts and fishing rod blanks, etc., to partly replace other reinforced fibers as a supplement to them. At first, when GRANOC™ low modulus carbon fibers were put onto the market, they were adopted mainly to reinforce the tips of shafts because such application could make full use of their characteristics. In recent years, more designs have been created for utilizing GRANOC™ low modulus carbon fibers for the entire length of golf club shafts and fishing rod blanks as a main

[*1] "GRANOC™" is a registered trademark of ENEOS Corporation that is the parent company of Nippon Graphite Fiber.

Table 1 Typical grade

GRANOC Grade	Fiber diameter	Tensile modulus	Tensile strength	Density	Thermal conductivity	CTE	Form		
	(μm)	(GPa)	(MPa)	(g/cm³)	(W/(m·K))	(10^{-6}/K)	Yarn	Chopped/ Milled	Fabric/ Prepreg
XN-05	10	54	1100	1.65	5	+3.4	○		○
XN-10		110	1700	1.70	–	−0.1	○		○
XN-15		155	2400	1.85	6	−0.8	○		○
XN-60		620	3430	2.12	180	−1.4	○		○
XN-80		780	3430	2.17	320	−1.5	○	○	○
XN-90		860	3430	2.19	500	−1.5	○	○	○
XN-100		–	–	2.22	900	–		○	
YSH-50A	7	520	3830	2.10	120	−1.4	○		○
YSH-60A		630	3830	2.12	180	−1.4	○		○
YSH-70A		720	3630	2.15	250	−1.5	○		○
YS-80A		785	3630	2.17	320	−1.5	○		○
YS-90A		880	3530	2.18	500	−1.5	○		○
YS-95A		920	3530	2.20	600	−1.5	○		○

Table 2 Properties of low modulus carbon fiber and other fibers

Fiber designation				GRANOC			PAN-CF	GF	Aramid
				XN-05	XN-10	XN-15	230 GPa	T-glass	Kevlar 49
Fiber properties	Tensile	Strength	(MPa)	1100	1700	2400	4900	4600	3400
		Modulus	(GPa)	54	110	155	230	83	130
	Elongation		(%)	2.0	1.7	1.6	2.1	5.5	–
	Density		(g/cm³)	1.65	1.70	1.85	1.80	2.49	–
Composites properties	0° Tensile	Strength	(MPa)	640	1050	1400	2800	1900	1380
		Modulus	(GPa)	34	72	93	137	49	76
		Strain to failure	(%)	1.8	1.5	1.4	1.8	3.9	–
	0° Compression	Strength	(MPa)	870	1070	1150	1400	970	276
		Modulus	(GPa)	32	64	85	129	55	–
		Strain to failure	(%)	2.9	2.1	1.8	1.4	1.8	–
	Comp. strength/Tensile strength ratio			1.36	1.09	0.79	0.50	0.51	0.20

Composites properties are based on epoxy resin prepreg for fiber volume of 60%.

material. Although steel is mainly used for wedge shafts, the number of carbon shafts is increasing as is the case with drivers and woods. For approach shots requiring delicate control, the weight balance and rigidity of shafts affect the spin rate and the controllability of the drive angle. To optimize these factors, laminate configuration where a thick layer of GRANOC™ low modulus carbon fibers is arranged in the outer layer sections of the shafts has been adopted. In addition, due to the impact sensation unique to carbon shafts, they realize a completely different drive sensation to that of glass fiber and steel shafts. Moreover, also regarding offshore casting rods for large migratory fish, laminate configuration where a thick layer of GRANOC™ low modulus carbon fibers is arranged for the entire length of blanks has been adopted. With regard to fishing targeting powerful, speedy fish (e.g., bluefin tuna), rod blanks need to have multiple functions, such as flexibility, repellency, bending strength, and weight balance. For rods designed with PAN-based carbon fibers, although they are lightweight, the repellency is too high; meanwhile, for rods designed with glass fibers, although they are flexible, the maneuverability is poor because they are heavier and thereby they tend to tire users. When GRANOC™ low modulus carbon fibers are applied, the adjustment range of the rigidity is wide and also their laminated materials have fracture elongation exceeding PAN-based fibers and bending strength surpassing that of glass fibers. These characteristics enable blank design that cannot be realized by glass fibers and PAN-based carbon fibers. In addition, using carbon fibers for blanks in place of glass fibers makes it possible to promote the product image itself to consumers as one of high class, in addition to the enhanced performance.[4, 5]

As described above, the ways to use GRANOC™ low modulus carbon fibers and their applications are increasing thanks to their unique characteristics that glass fibers and PAN-based carbon fibers do not have. In addition, as the sports equipment market develops, many of the existing manufacturers are shifting their development focuses to high-grade products with advanced amateur, semiprofessional, and professional specifications because such products make it easier to secure the profitability. This fact also works to accelerate the replacement of glass fibers and other types of fibers with GRANOC™ low modulus carbon fibers. Under such circumstances, GRANOC™ low modulus carbon fibers are expected to further dramatically grow as an optional material that supports increase in the performance of sports equipment in the future as well.

3.2 High modulus grade

3.2.1 High rigidity and excellent vibration damping property

The high modulus carbon fibers manufactured by Nippon Graphite Fiber have elastic moduli of 520 to 920 GPa. When our high modulus carbon fibers are combined with thermosetting resin, the specific modulus (value obtained by dividing the elastic modulus by the density) of the obtained CFRP is approximately ten times that of aluminum and steel and approximately 2.5 times that of PAN-based CFRP. The specific modulus is used to evaluate and compare the mechanical properties of materials. Thus, the CFRP is an ultra-lightweight material having high rigidity (**Fig. 3**). In addition, the deflection of CFRP involving high modulus carbon fibers can be controlled to very low. We designed beams in the same size manufactured from different materials and simulated the deflection when one end is fixed and a uniform load is applied to the top. **Figure 4** shows the simulation results. Regarding the beam for which high modulus carbon fibers with a high specific modulus are arranged in one direction, the deflection due to its own weight (deflection by own weight) and the deflection due to the uniform load (deflection by load) can be controlled to a minimum; the deflection can be suppressed to be approximately one quarter that of steel and one fifth that of aluminum. In addition, its vibration damping property is higher thanks to its high natural frequency compared with the other structural elements. **Figure 5** compares the vibration damping property of PAN-based CFRP with that of pitch-based high modulus CFRP. The vertical axis is the amplitude and the horizontal axis is the damping time. The figure shows that the amplitude of the pitch-based high modulus CFRP settles in a shorter time compared with the PAN-based CFRP.

Industrial high-rigidity, high-speed CFRP rolls are a typical application for which the lightness, high rigidity, and excellent vibration property are fully used. As the electrification of vehicles accelerates, there is increasing demand for CFRP rolls for equipment for manufacturing high-functionality films, such as LIB separator films and films for automotive multilayer ceramic capacitors, in addition to existing printers and resin film production equipment. In addition, high-rigidity, high-speed CFRP rolls also play an important role toward the practical implementation in the printed electronics field, represented by flexible displays and flexible solar cells, which are gaining attention as the next-generation technologies.

CFRP components have also been increasingly adopted for high-speed operation equipment, for example, electronic component mounters used in semiconductor chip manufacturing processes. Equipment to be used to mount several tens of submillimeter-sized electronic components at designated locations on substrates per second must have high-accuracy positioning control that does not permit deviation at the micrometer scale. Accordingly, components involving lightweight high modulus pitch-based carbon fibers with high rigidity and an excellent vibration damping property are appropriate.

As typical applications for sports and leisure, there are road bicycles designed for competition, which are used by top cyclists who are active in the Tour de France and other cycling race categories, and gravel road bicycles, which have become popular in recent years. Load deformation of bicycle frames, which tends to occur during acceleration, hinders the conversion of the driving force by pedaling into force for propelling the bicycles. To prevent this, as shown in **Fig. 6**, high modulus carbon fibers are being intensively

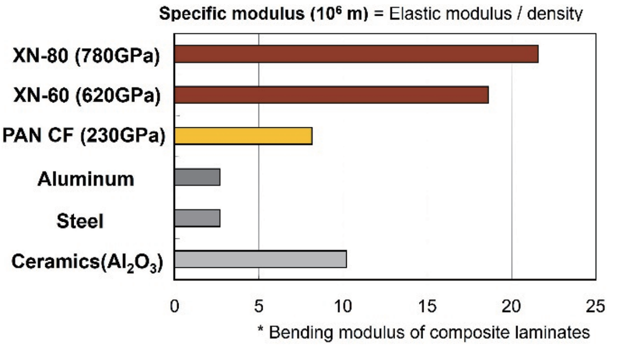

Fig. 3 Specific modulus of CF laminates in comparison with different materials (XN-80 and XN-60: Pitch-based high modulus CF laminate)

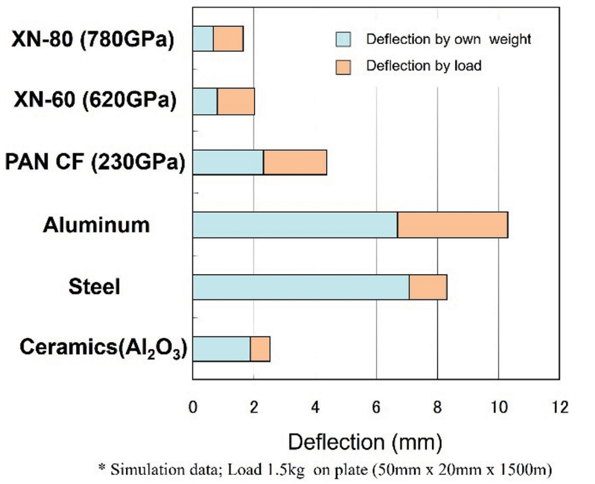

Fig. 4 Comparison of the deflection of beams made of different materials (XN-80 and XN-60: Pitch-based high modulus laminate beams)

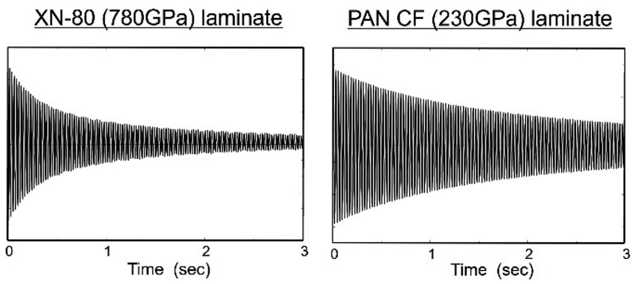

Fig. 5 Vibration damping properties of pitch-based, and PAN-based laminate

used for the frame section near the head tube and bottom bracket to which loads are applied in particular, realizing both higher rigidity and lighter weight. Carbon frames are manufactured by internal pressure molding (where carbon fiber prepreg sheets are laminated inside molds and frames are formed while the molds are heated). However, applying high modulus carbon fibers to complicated shapes involving a curved surface is regarded as difficult, in general, because the fibers tend to bend and crimp. In fact, the GRANOC™ YS/YSH grades manufactured by Nippon Graphite Fiber have the narrowest fiber diameter among pitch-based carbon fibers and high

Fig. 6 Example of using YSH-60A fiber to stiffen ultralight road bicycle frames

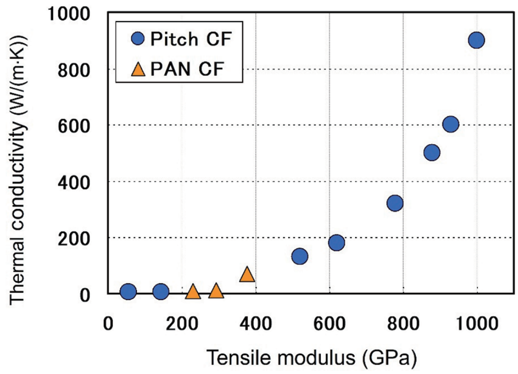

Fig. 7 Relationship between the tensile modulus and the thermal conductivity in the fiber direction of carbon fibers

flexibility and thereby they can be well formed into complicated die shapes and fiber breakage and crimps during internal pressure forming can be suppressed. The GRANOC™YS/YSH grades can produce high-reliability, high-safety composites. At the beginning of the 2000s, the adoption of GRANOC™YSH-60A (with an elastic modulus of 630 GPa) products for bicycle frames began and currently, it is used for many of the lightest carbon frames. We will promote customer support toward the application of the GRANOC™ YS/YSH grades having elastic moduli of 720 and 785 GPa to further improve the rigidity of bicycle frames and reduce their weight.

3.2.2 High thermal conductivity

As the elastic modulus of pitch-based high modulus carbon fibers becomes higher, the growth of graphite crystals increases and the orientation becomes higher. Accordingly, the elastic modulus and thermal conductivity (TC) have a positive correlation (**Fig. 7**). Nippon Graphite Fiber provides multiple grades and product forms having different TC and thereby it can introduce products that match the manufacturing processes of customers and the specifications of ultimate products.

Figure 8 shows the in-plane heat transfer visualized with a thermal imaging camera for composites for which the typical GRANOC™ XN-60 (fiber: TC = 160 W/(m·K), composite: TCxy = 60 W/(m·K)), GRANOC™XN-80 (fiber: TC = 320 W/(m·K), composite: TCxy = 90 W/(m·K)), and GRANOC™XN-90 (fiber: TC = 500 W/(m·K), composite: TCxy = 135 W/(m·K)) were used along with an aluminum alloy (TCxy = 140 W/(m·K)) in the same size. The higher the elastic modulus of carbon fibers, the higher the TC in the fiber direction. Accordingly, the figure shows that the distances of heat transmission from the heat sources are longer in the order of XN-90, XN-80, and XN-60. When compared with the aluminum alloy (different material), the heat dissipation property of the aluminum alloy is similar to that of the XN-90 composite. Because aluminum alloys are a lightweight and high-thermal conductive component, they are used for electronic component enclosures involving heat generation and heat sinks, etc. Now, replacing aluminum alloys with lightweight, high modulus carbon fibers having high rigidity and thermal conductivity is being considered.

Thermoplastic prepreg NS-TEPreg™ of Nippon Steel Chemical & Material Co., Ltd. was combined with XN-80. By fully using the excellent physical properties of resin, ease of forming, and mass productivity of NS-TEPreg™ as well as the high rigidity and high thermal conductive property of XN-80, we are proposing the material for cases and parts of notebook computers, tablets, smartphones, and cameras that must be lightweight and have high rigidity and heat dissipation. The material has been adopted for D covers (the

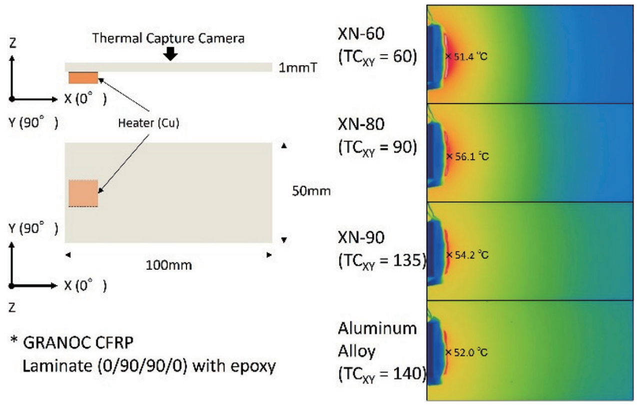

Fig. 8 Comparison of heat dissipation properties of pitch-based laminate

Fig. 9 Ultralight and high stiffness laptop with XN-80 fiber (LAVIE PRO MOBILE)[6)]

face of case bottoms) of the LAVIE PRO MOBILE model of NEC Corporation, contributing to realizing a thinner and lighter model and mitigating local temperature increase, which tends to occur on the bottom (**Fig. 9**[6)]).

Some issues have arisen with heat generation from equipment installed at cell sites as the transfer to the next generation mobile communication system 5G proceeds as well as from in-vehicle electrical components as autonomous driving and EVs spread. Pitch-based high modulus carbon fibers have been increasingly adopted as solutions for such heat generation issues and the utilization as such solutions is being considered. Short fiber products (chopped and milled fibers) with TC of 600 to 1200 W/(m·K), in particular, are

Table 3 Properties and applications of GRANOC

Grade	Property	Application			
		Industrial	Sports & Leisure	Satellite & Aerospace	Thermal management
Low Tensile modulus	Light weight		Golf shaft		
	Flexibility		Fishing rod		
	Excellent impact resistance		Badminton racket Tennis racket Hockey stick		
High Tensile modulus	Light weight	Roller	Golf shaft	Antenna, reflector	Thermal interface material
	Low deflection	Robot hand	Fishing rod	Solar array	Laptop case
	Low vibration	Drive shaft	Ski pole	Optical bench	C/C brake
	Dimensional stability	Construction repair	Bicycle frame	Telescope tube	Ceramic brake
	High thermal conductivity	and reinforcement		Bus, payload	
	Radiolucency	Acoustic diaphragm		Support structure	
	Sliding characteristic	X-ray medical tabletop X-ray cassette			

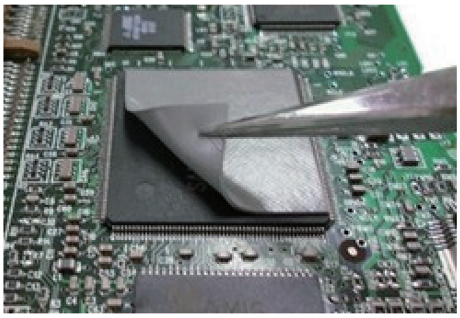

Fig. 10 High thermal conductive silicone sheet with high thermal conductive pitch-based carbon fiber

charged into an organic binder system (e.g., silicone resin) along with high-thermal conductive ceramics and metal fillers to produce heat dissipation sheets[7, 8] as products that realize both flexibility and a thermal conductive property (**Fig. 10**). Putting heat dissipation sheets between heating elements (e.g., semiconductor devices) and radiators (e.g., heat sinks and heat pipes) can propagate heat uniformly.

4. Conclusion

Lightweight pitch-based carbon fiber GRANOC™ products with wide-ranging elastic moduli have characteristics that cannot be obtained from other materials, in addition to the characteristics described above; GRANOC™ products make it possible to design components with an excellent sliding property, high X-ray transparency, small thermal expansion coefficient, and high dimensional stability. **Table 3** lists the properties of the GRANOC™ fibers and their applications that fully utilize the properties. We are determined to work hard to improve the product quality and properties as materials that will also contribute to technical innovation in various fields in the future.

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