JACI Textbook | Learning from social practice cases that have received the GSC Awards

Green and
Sustainable
Chemistry

Introduction to GSC

No.3 Revised Edition

Received the Minister of Economy, Trade and Industry Award of the 13th GSC Awards (2013)

Development of Carbon Fiber Composite Materials for Lightweight Commercial Airplanes

Toray Industries, Inc.

Toray Industries, Inc. have developed carbon fiber-reinforced plastic (CFRP), a composite material that enables the fabrication of lightweight airplane structures.
Reducing the weight of an airplane permits the carriage of more passengers and cargo and extends the flight distance.
A lightweight airplane conserves energy, causes low CO_2 emissions, and minimizes the emission of greenhouse gases that cause global warming.

Outline of the GSC Awards and the award-winning company

The GSC Awards are bestowed upon individuals and organizations for their contribution toward the advancement of Green and Sustainable Chemistry (GSC), and several awards are conferred each year. Innovations that contribute toward the development of sustainable industrial technology are awarded the Minister of Economy, Trade and Industry Award; those that contribute toward the development and promotion of science are awarded the Minister of Education, Culture, Sports, Science and Technology Award; those that contribute toward the overall reduction of environmental impact are awarded the Minister of the Environment Award; while small and medium-sized businesses that contribute toward the development of industrial technology are awarded the Small Business Award (established in 2015; renamed to Venture Company Award, Small and Medium-sized Company Award in 2018 and Venture, Small and Medium sized Company Award in 2022). Additionally, innovations that exhibit high potential for future development are awarded the Incentive Award.

Toray Industries, Inc. is a chemical manufacturer (Head Office: Chuo-Ku, Tokyo) founded in 1926. TORAY's business covers chemical products including synthetic fibers and synthetic resins, and information-related materials.

Objective of the textbook series

Global issues, in areas such as resources and energy, global warming, water and food have increasingly become major and complicated concerns. Innovations for achieving both environmental conservation and economic development are needed in order to resolve these issues and realize the sustainable development of society, and expectations for GSC continue to rise. In this textbook series, technologies and products that have received the GSC Awards given to great achievements contributing to the progress of GSC are explained, so that everyone can understand "what is GSC?" and take responsibility for realizing a sustainable society.

*Please refer to The Statement 2015 at the end of the textbook.

What is GSC?

Acronym for Green and Sustainable Chemistry

Definition of GSC

Chemical sciences and technologies which are benign to both human health and the environment, and support the development of a sustainable society

Guidelines of GSC activities

- The chemistry community has been addressing future-oriented research and education, and development towards environmentally-benign systems, processes and products for the sustainable development of society.

- Specifically, in response to the Rio Declaration at the Earth Summit in 1992, the chemistry community has been working in a unified manner linking academia, industry and government to start up Green and Sustainable Chemistry and engage in its activities, in order to advance the pursuance of coexistence with the global environment, the satisfaction of society's needs, and economic rationality. These goals should be pursued with consideration for the environment, safety and health across the life cycles of chemical products, their design, selection of raw materials, processing, use, recycling and final disposal.

- Long-term global issues, in areas such as resources and energy, global warming, water and food, and demographics have increasingly become major and complicated concerns in the present century. Therefore, expectations are growing for innovations, based on the chemical sciences, as driving forces to solve such issues and to achieve the sustainable development of society with enhanced quality of life and well-being.

- The chemistry community will live up to these expectations by strongly advancing Green and Sustainable Chemistry through global partnership and collaboration and by bridging the boundaries that separate industries, academia, governments, consumers and nations.

Examples of GSC

- The general classification is expressed in terms of a combination of the intended social contribution and the means to achieve this goal. With regard to the objectives, the efforts to achieve them have extended in stages from social challenges to difficult long-term challenges, beginning with manufacturing or utilization, and common/basic categories have also been established -

Minimization of resource consumption and maximization of the efficiency of reaction processes for production with reduced environmental impact

1. Chemical technologies and products that lead to reduction in by-product formation and avoid the use of hazardous substances

2. Separation, purification and recycling technologies that reduce the generation and emission of greenhouse gases like CO_2 or toxic/hazardous substances, thus lowering environmental impact

3. Chemical technologies and products that reduce the generation and emission to the environment of greenhouse gases like CO_2 or toxic/hazardous substances

4. Catalysts and reaction processes that realize the saving of energy and resource and improvement in product yields

Risk reduction of chemical substances beneficial to safe and secure living environment

5. Chemical technologies, products and systems that reduce waste generation

6. Chemical technologies, products and systems that inhibit the generation and emission of hazardous substances and pollutants

Challenges to solve energy, resource, food and water issues

7. Chemical technologies, products and systems to utilize low-grade heat sources, non-conventional resources, and other similar alternatives

8. Chemical technologies, products and systems whereby un-utilized energy and resources can be converted into available energy, transported and stored

9. Chemical technologies, products and systems which decrease the dependence on exhaustible resources such as fossil fuels and scarce minerals and promote the shift to renewable energy and resources, including their storage

10. Chemical technologies, products and systems that contribute to the Three R's: Reduce, Reuse and Recycle

11. Chemical technologies, products and systems that promote the efficiency of production and supply of food, and utilization of water resources

Pioneering challenges to long-term issues aiming to realize a safe, secure and sustainable society with enhanced quality of life

12. Chemical technologies, new products and new operational systems that contribute to the introduction of new social systems, for instance based on ICT, and aimed at solving social issues such as energy and resource consumption, food and water security, disaster prevention and infrastructure improvements, transportation and logistics, medical and health care, education and welfare, and other mega-trends of society

13. Chemical technologies, new products and new operational systems that contribute to the improvement of social and individual comfort whilst reducing and preferably inhibiting environmental impact

Systematization, dissemination, enlightenment and education of GSC including its metrics to be established

14. Systematization of GSC practices and concepts

15. Dissemination, enlightenment and education of GSC practices and concepts

16. Establishment and dissemination of GSC metrics

(Definition from JACI GSCN Council
https://www.jaci.or.jp/english/gscn/page_01.html)

Weight reduction of airplanes using carbon fiber composite materials, realized at last by cooperation and strong conviction over the generations

Toray Industries, Inc.

The Minister of Economy, Trade and Industry Award of the 13th GSC Awards (2013) was given to the “Development of Carbon Fiber Composite Materials for Lightweight Commercial Airplanes” by Toray Industries, Inc. TORAY’s carbon fiber reinforced plastic (CFRP) developed through over 40 years of research and development has features of high toughness (material tenacity) in combination with light weight and flexibility. High-toughness CFRP enables the construction of lightweight airplanes with improved fuel consumption, which contribute substantially toward reducing the environmental impact of aviation.

Fig. 1: Carbon fibers, intermediate products (woven cloth and pre-preg), and products (CFRPs) for commercial application

1 The Path to Technology Development

(First step in Open Innovation*1)

~ What were the intentions that started development toward realizing the sustainable progress of society?

*1
Open Innovation: " Open Innovation" is a business model for creating innovative values, typically including development of new products by incorporating technologies and ideas owned by various outside sources such as other companies, universities and research institutes, and combining them with one's own technologies and ideas.

*2
Elasticity/elastic modulus: Elasticity is the ability of an object to regain its original state after the removal of an external deforming force. The elastic modulus is the ratio of a resisting force to this deformation (strain), and a higher value indicates higher resistance to deformation.

Carbon forms substances of various forms by atoms bonding successively mainly through covalent bonds. Carbon materials such as diamond and graphite formed by the carbon are used in various industries, and their application fields are continuously expanding (Column①).

Carbon fiber is also one of such carbon materials. The specific gravity of carbon fiber is 1/4 in comparison with steel, and in view of the unit specific gravity, the strength of the carbon fiber is higher by approximately 10 times and the deformation resistance (elastic modulus)*2 is higher by approximately 7 times. Thus, carbon fibers are "stronger than steel and lighter then aluminum," and show excellent resistance to corrosion and fatigue. The carbon fibers are not used alone but are usually mixed into plastic, rubber, metal or concrete to be used as a "carbon fiber composite material." In these composites, the incorporation of carbon fiber improves the strength, electrical conductivity, and heat resistance of the original material. For example, in addition to the products shown in Fig. 1, the carbon fiber is used for shafts of golf clubs and fishing rods, and reinforcement of reinforced concrete for earthquake resistance and fireproofing (Fig. 1). Among the different types of carbon-fiber composite materials, the high-toughness CFRP used in the construction of the medium-sized passenger airplane "Boeing 787" by The Boeing Company, which significantly reduces the weight of the airplane structure, is particularly interesting.

Fibrous carbon materials have a long history. For example, bamboo-derived carbon materials were used as a filament in light bulbs which were put into practical use by Edison in the 19th century. Thereafter, light-bulb filaments were replaced by tungsten. However, in the 1950s, carbon fibers regained prominence on being used as jet-orifice materials in rockets.

At that time, products made of carbon and graphite were limited to molded products such as electrodes, or powdery products such as activated carbon and carbon black. The production of fibrous graphite was considered to be difficult. In 1956, Union Carbide Corporation in the United States succeeded in developing the world's first carbon fiber by using rayon as a precursor material.

Around that time, Dr. Akio Shindo, a researcher (joined in 1952) of the Osaka National Research Institute of the Agency of Industrial Science and Technology (present Kansai Center in National Institute of Advanced Industrial Science and Technology), was searching for new carbon materials with a desire to "be useful to society." In the process, Dr. Shindo came upon a newspaper article on carbon fibers related to graphite felt, etc. He perceived that "this will lead to innovation," and immediately started research aimed at the industrialization of carbon fibers.

In order to efficiently obtain carbon fibers, it was necessary to find a precursor material having a fibrous form which maintains the fibrous form and constitutes only carbon atoms even after being subjected to heat treatment. The utilization of carbon materials as carbon-fiber precursor materials requires extremely high energy (the melting and stretching of carbon materials involves covalent-bond breakage); therefore, this process is unrealistic. On the other hand, synthetic fibers that had already been put into practical use at that time were fibers that mainly contain carbon atoms, and therefore suitable as precursors for carbon fibers.

Therefore, Dr. Shindo attempted to convert different types of synthetic fibers into carbon fibers. However, he had difficulty in converting the materials into carbon fibers, because the heat treatment caused some materials to disperse like mist, and others to melt before carbonizing, etc. One day, he noticed that the list showing properties of synthetic fibers indicated that many fibers decompose and melt under heat treatment, whereas only polyacrylonitrile (PAN)*3 fibers become "tenacious at 235°C." This meant that PAN fibers have heat resistance, and could be carbonized while keeping the fibrous form.

By repeating experiments using the obtained PAN fibers, Dr. Shindo finally produced PAN based carbon fibers that were flexible enough to be wrapped around the finger. He repeatedly examined the heat-treatment temperature, oxidizing atmosphere, and tension of PAN fibers to stably manufacture large amounts of carbon fiber. Blessed with serendipity (accidental discoveries), he finally published these results in a paper in 1961. At the same time, he filed a basic patent in 1959, which served as a basis for the future

Thereafter, while the results became known to worldwide researchers, one researcher's opinion that "fibers with high specific modulus are promising as reinforcing fibers for composite materials" prompted the promotion of research and development of carbon fibers as structural materials and research and development of composite materials (CFRP: Carbon Fiber Reinforced Plastic) with resin (Column ②).

On heating, PAN fibers are converted into carbon fibers with a strong graphite-crystal structure (Fig. 2 and 3) owing to intermolecular-bonding changes. PAN-based carbon fibers differ from rayon-based carbon fibers; they contain fused benzene rings that are regularly aligned in the direction of the fiber, which impart high strength and elastic modulus to the structure (Column ③).

*3
Polyacrylonitrile: a polymer of acrylonitrile. Polyacrylonitrile is the main component of acrylic fibers. Acrylic fibers are obtained by copolymerizing acrylonitrile with vinyl acetate, etc., and have a texture similar to wool.

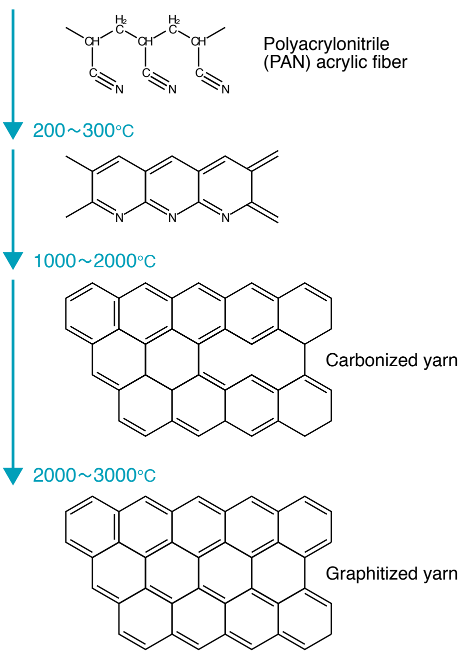


Fig. 2: Formation of carbon fibers from polyacrylonitrile
Heating polyacrylonitrile within 200–300°C generates a cyclic structure, heating within 1,000–2,000°C eliminates all elements other than carbon and generates strong carbon fibers, whereas heating within 2,000–3,000°C causes graphitization (see "In More Detail" on page 11).

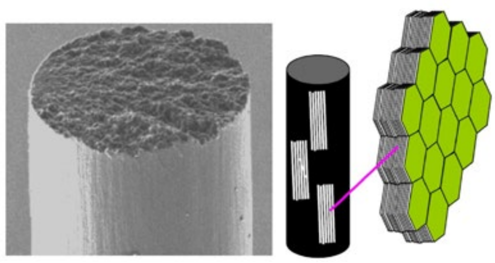


Fig. 3: Structure of carbon fibers

2 Toward Resolution of Issues

(Second step of Open Innovation)

~ What types of technological challenges did the developers face and how did they resolve them?

Success in industrial production of carbon fibers (1970s~)

After the development of a method for synthesizing carbon fibers using PAN-based fibers, several companies began manufacturing carbon fibers. However, the long manufacturing time and high cost of the process prevented industrial production. Toray Industries, Inc. (hereinafter referred to as "TORAY") was one of many companies that focused on the carbon fibers. TORAY was originally a fiber manufacturer, and thus mainly advanced the research on PAN fibers for carbon fibers.

Hydroxyethyl acrylonitrile (HEN), a compound that is structurally similar to acrylonitrile (the starting material for PAN fibers), was discovered during nylon-production research at the Basic Research Laboratory in TORAY. This new compound HEN has an effect of promoting oxidation[*4] of PAN fibers, and it was found that mixing with PAN produced carbon fibers with excellent mechanical properties.

TORAY took this opportunity to start a project aimed at producing its own carbon fibers. In 1970, after obtaining permission to use a basic patent for the production of carbon fibers using PAN, TORAY began full-scale industrialization. However, with no technology for carbonizing (heat treatment) large quantities of PAN fibers, TORAY approached the Union Carbide Corporation for technology exchange and acquiring knowledge on carbonizing fibers.

TORAY started the commercial production of carbon fibers in 1971. This initiated the major lead of Japanese companies in the production of PAN-based carbon fibers against Western companies in later years. However, owing to limited knowledge regarding the utility and applications of carbon fibers, the carbon-fiber market was not a growing market at the time.

TORAY aimed to immediately start using carbon fibers in airplanes owing to the high strength and elastic modulus of CFRPs. However, certification by airplane manufacturers took a significant amount of time.

TORAY pioneered the carbon-fiber market through trial and error to maximally expand the use of carbon fibers. FRP-based fishing rods gained popularity due to their lighter weight compared to conventional glass-fiber fishing rods, and the use of carbon fibers expanded to sports equipment such as golf club shafts and tennis rackets, for which high prices are more acceptable as long as they deliver high performance.

At the same time, TORAY advanced improvement in the performance of carbon fibers. Consequently, carbon fibers manufactured by TORAY became widely recognized as "lightweight and strong." In 1978, these carbon fibers were finally certified as airplane material by The Boeing Company.

*4
Oxidation treatment: This treatment is carried out by heating the precursor fibers in an oxygen-existing atmosphere to avoid fusion of the fibers upon carbonization.

To make airplanes more lightweight and stronger with carbon fibers (1990s~)

In general, to guarantee the safety of an airplane structure, new materials are first used in low-risk components (nonstructural materials). They are used in components that support the load as a mainframe (structural materials) only after validation.

CFRPs underwent a similar process. First they were used as nonstructural materials (such as interior materials), and then as structural materials (first in secondary components, such as control surfaces, and finally in primary components, such as the main wings and fuselage). In 1986, The Boeing Company proposed the required specifications for certifying CFRP as the primary structural material responsible for the strength of the airplane.

The basic structure of conventional airplanes comprises an aluminum alloy with high processability, toughness[*5], strength, lightweight properties, corrosion resistance, and material costs. An innovative material was required for realizing further weight reduction. Thus, high expectations were held for CFRP, which made a quantum jump in lightweight property and strength (Fig. 4) and was free of corrosion, as

*5
Toughness: Tenacity of the material. A property that is not easily destroyed by external forces.

the primary structural material.

Resin which gives shape and toughness to CFRP is referred to as the matrix, and carbon fibers which give strength is referred to as the reinforcement.

The carbon fibers used as the reinforcement were designed based on deep and elaborate analysis in property controlling factors, and high-strength, high-elastic modulus carbon fibers were developed.

To manufacture airplane structures using carbon fibers, an intermediate material, pre-preg (Fig. 1), was used as the base material. The pre-preg is a sheet material in which carbon fibers are aligned in one direction and a thermosetting resin is impregnated therein. To fabricate airplane structures, several sheets of pre-preg were stacked to form a specific shape, followed by the application of pressure and heat in an oven (autoclave) to cure the resin.

CFRP, in which carbon fibers being the reinforcement are aligned in one direction, is strong in the fiber direction but is weak in the transverse direction of the fiber. Therefore, sheet-like prepregs as shown in Fig. 1 are stacked in multiple and optimum directions against the applied external force to form the structure. Although this laminated structure can be strengthened in any planar direction, the toughness of the material must be improved to reduce delamination between the laminated sheets.

Airplanes are operated under extreme conditions. If a large hailstone strikes the airplane in cold climate, the aluminum alloy currently used receives a strong impact that will cause damage in the struck area. Moreover, sand and rocks strike the airplane during take-off and landing. As mentioned previously, CFRP materials may exhibit typical delamination damage on impact. It is crucial to maintain this damage below a design-allowable level.

While designing composite materials, the carbon fibers (as reinforcement) and matrix should both be meticulously designed. The epoxy resin typically used as the CFRP matrix exhibits excellent adhesion and chemical resistance, and its properties can be modified by changing the additives used with the base resin. Joining of the sheets takes place between the matrices, and thus the issue of improving toughness against delamination between the sheets became the issue of epoxy resin*6 as the matrix.

A difficulty encountered during the research for increasing toughness of the epoxy resin itself as a matrix was the trade-off relationship between toughness and strength in CFRP. To meet the airplane-structural-material criteria proposed by Boeing, this issue required resolution.

A breakthrough came by an idea of improving only the portion where the fracture occurs, instead of uniformly improving the entire matrix. Epoxy resin was used to maintain the overall strength of the CFRP material, while thermoplastic-resin particles were arranged between the fracture-susceptible regions of the sheets for additional toughness (Fig. 4). By doing so, when an impact is applied to the surface of the CFRP, the thermoplastic particles become deformed, some particles break to absorb energy, and therefore the propagation of cracks can be suppressed.

To achieve this target, TORAY developed its own thermoplastic particles. Mr. Makoto Endo, Director of TORAY's Composite Materials Research Laboratories, who was involved in their development, recounts the following:

"The reason why we were able to create such an innovation was that the target of development was a composite material, which required a team of experts from various fields, such as physics, organic chemistry, material mechanics, and polymer chemistry. Once the team members understand each other's different perspectives, that stimulation leads to unexpected ideas."

TORAY's high-toughness CFRP was certified in 1990 as the primary structural material for the empennage and floor beams of the Boeing 777.

*6
Base resin and additives for epoxy resins: The most well-known bisphenol A type epoxy resin is obtained by reacting bisphenol A and epichlorohydrin, and the properties of the epoxy resin can be further modified by using various additives. Various combinations of base resins and curing agents are currently in use.

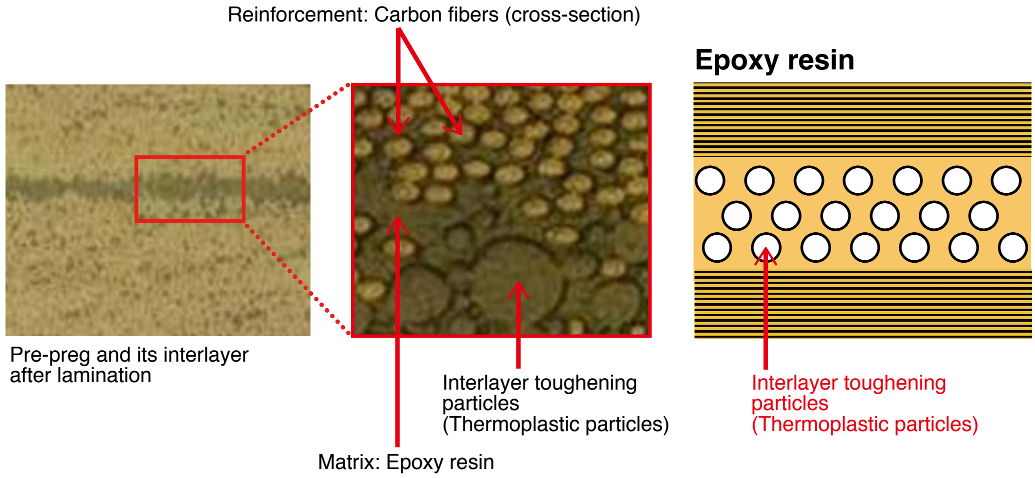


Fig. 4: Cross-section of a pre-preg laminate

*7
Spinning: A process of obtaining fibers by turning a raw material into liquid and extruding the liquid from a spinneret (nozzle) to produce synthetic fibers. The three methods for producing general purpose fibers are the "melting method,", "dry method" and "wet method." The melting method is a method in which the polymer is melted by heat and extruded from the spinneret into a fibrous form, which is then cooled and hardened. In the wet method, the polymer is extruded through numerous holes into a coagulation liquid to produce a yarn. In the dry method, the polymer is extruded through a number of holes and the solvent is evaporated to solidify the fabricated material. The final PAN-based carbon fibers form a bundle of long fibers (filaments) with a diameter of 5–7 micrometers (μm).

*8
Specific strength: strength per unit specific gravity

*9
Specific modulus: Evaluated by dividing the elastic modulus by specific gravity. It represents the elastic modulus per unit specific gravity (*2). Materials that are both lightweight and exhibit a high elastic modulus show a high specific modulus. The specific strength is obtained by dividing the strength by the specific gravity. It represents the strength per unit specific gravity. The specific gravity of PAN-type carbon fibers lies within 1.74–1.95.

Toward mass production (from the 2000s)

Low production cost is a prerequisite for the widespread and abundant use of materials. Consequently, to facilitate the low-cost mass production of carbon fibers for CFRP, TORAY attempted to improve the productivity of the carbon-fiber manufacturing strategy. Conventional production methods involve numerous time-consuming processes and are unsuitable for mass production. Without changing the fundamental strategy, TORAY thoroughly revamped the entire synthesis process, including the synthesis of yarn (the carbon-fiber precursor), and reduced the total number of steps.

Consequently, the revamped spinning*7 method was developed by TORAY. This method comprises a dry-wet spinning method that combines the low-cost wet method with the high-quality dry method for high-speed carbon-fiber production. In this method, a gap is provided between the spinneret and the bath where the coagulant is retained, and the raw material is deformed in the gap while being extruded into the coagulant to form the yarn.

TORAY realized high speed operation by the new spinning method, and improved productivity by a technology which enables uniform fiberization even if the number of fibers to be produced at one time is doubled from 12,000 filaments to 24,000 filaments. The orderly production of a large number of microfibers requires advanced production techniques. TORAY could develop this advanced method owing to the availability of technology to control fiber spinning.

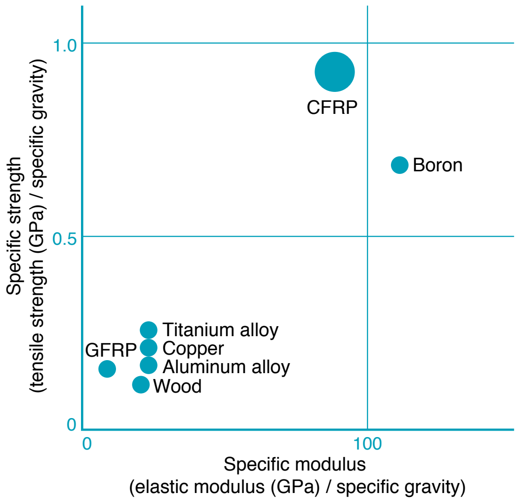


Fig. 5: Comparison of the specific strength*8 and specific modulus*9 of CFRP with those of other materials (including metals)
(Akihiko Kitano, Chemistry & education, 59 (4), 228 (2010))
CFRP exhibits a higher specific strength and specific modulus than other materials.

3 Contribution to Society

~ What is the contribution of this novel technology to society?

Approximately 60 years have passed since basic research on carbon fibers began under Dr. Shindo of the former Osaka Industrial Research Institute. The carbon-fiber market has grown into an industry that covers approximately 80% of the world market (in terms of production by Japanese companies). Carbon fibers manufactured by TORAY occupy a global market share of approximately 50%.

Carbon fibers were first used in airplanes in 1975 (to fabricate the interior components of the Boeing 737). Carbon fibers were used in the airplane structure for the first time in 1983, and in the empennage and floor beams of the Boeing 777 in 1992. Approximately 7 tons of carbon fiber were used per airplane. Furthermore, in 2003, high-toughness CFRP was extensively used for the main wings and fuselage of the Boeing 787 (Fig. 5). In 2006, the production of the Boeing 787 was initiated, resulting in the fabrication of a "black airplane."

In Boeing 787, the amount of carbon fibers used per airplane was about 35 tons, and the weight of the airplane was considered to be

20% lighter than the conventional airplane.

Carbon fibers, owing to their production method, exhibit a higher material-production energy per unit weight than metals such as steel. Therefore, the LCA perspective is important for a proper analysis of carbon fibers. LCA is a technique for comprehensively evaluating the environmental impact of a product throughout its life cycle (from resource collection to product design, production, use, recycling, and disposal) (see Introduction to GSC No. 1). According to CO_2-emission calculations of the Japan Carbon Fiber Manufacturers Association, carbon fibers are expected to significantly reduce the CO_2 emissions from airplanes.

In the Boeing 787, CFRP comprises 50% of the weight of the airplane structure. Model calculations using the same CFRP composition ratio on the Boeing 767 (an existing airplane comprising an aluminum alloy) indicate a 7% reduction in CO_2 emissions in the entire life cycle of the product during 10 years of operation. For Boeing 767-class airplanes, the percentage of CO_2 emission during operation relative to the total CO_2 emissions from standard domestic services during the period from the production of the material to the scrapping of the airplane reaches up to 99%. Therefore, an improving fuel efficiency through weight reduction is a direct effect of reducing CO_2 emissions.

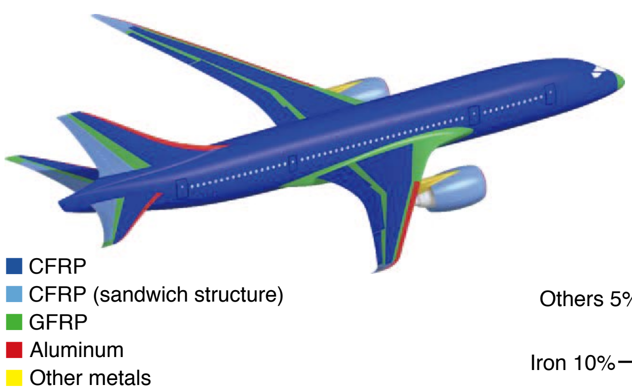
The entire world focused attention on carbon fibers, and many companies took on the challenge but most of them gave up development. Even so, the reason TORAY was able to patiently continue development of carbon fibers was because TORAY was confident that no other material had excellent properties like carbon fibers, and believed in their future prospects. Another reason was that researchers involved in the development had strong hopes of "flying a black airplane" by the use of black carbon fibers

The key to successful carbon-fiber innovation is collaboration: collaboration between government (industrial technology seeds) and private sectors (industrialization of technology seeds), between material manufacturers and airplane manufacturers, and researchers across specialized fields within the research team. Material manufacturers sometimes collaborate with parts manufacturers, but usually not with airplane manufacturers.

Mr. Endo states: "We and Boeing were not sure how to use this material because there was no precedent using the new material. Much discussion took place. Of course, we collaborated with parts manufacturers to develop processing technology. Innovation in materials and innovation in processing technology occurred in parallel."

Mr. Endo says that he will continue to pursue reducing the weight of airplanes. Although the Boeing 777X (an airplane larger than the Boeing 787) is in production, carbon fibers have not yet been used in small airplanes. The cost of carbon fibers must be reduced further for application in small airplanes.

According to Mr. Endo, "in the past, development was targeted on the goal of 'stronger and stiffer,' but from now on, we want to proceed with a comprehensive development to meet the user's needs." Today, the application of carbon fibers is expanding rapidly to ships and watercraft, civil engineering and construction, as well as automobiles and airplanes. The widespread application is expected to save energy and reduce environmental impact.



Seats: 200/250/300
Fuel efficiency: improvement by 20% over the same class
Range: 6,500 to 16,000 km
Speed: Mach 0.85
In service: since 2011
CFRP: about 35 tons per airplane

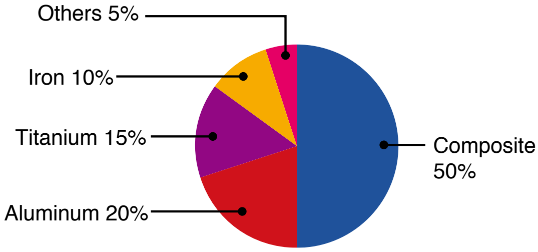


Fig. 6: Components using CFRP in Boeing 787 (Boeing Japan)
Only the carbon fibers and pre-preg manufactured by TORAY are certified for use as primary structural materials for the Boeing 787.

Column 1

Carbon materials

Carbon is an element with the atomic number 6, and forms substances of various shapes by atoms bonding successively through covalent bonds. Allotropes are substances that comprise the same element but exhibit different properties. Well-known carbon allotropes include diamonds, graphite, charcoal, soot, and coke. Graphite and diamond exhibit regular crystal structures, whereas charcoal and soot are amorphous carbons with no solid crystal structures.

Carbon materials have been historically used as fuel. The discovery of nanocarbons (substances comprising carbon with a diameter of approximately 10−9 m) such as fullerene, graphene, and carbon nanotubes at the end of the 20th century opened new frontiers in the applications of carbon materials. These carbon allotropes can be macroscopically classified into dot-shaped fullerenes, linear-shaped carbon nanotubes, and planar graphene.

Nanocarbons, the basic research theme that received the Nobel Prize in Chemistry in 1996 (fullerene) and the Nobel Prize in Physics in 2010 (graphene), are expected to exhibit wide applicability in several fields (such as chemistry, energy, and electronics) because of their light weight, high strength, and good electrical conductivity.

Column 2

A national-level innovation model

The National Institute of Advanced Industrial Science and Technology (AIST) evaluated this case as a successful innovation model. AIST has bridged the growth of Japanese companies to an industry that accounts for approximately 80% of the global market production through integrated full-scale research from basic research to commercialization (including the promotion of original research, development of the domestic industry based on basic patents, and standardization of the mechanical strength measurement of fibers). The success of this technology can be attributed to the combination of clear conceptualization, energetic research, serendipity organizational researcher support, and the industrial impetus for the development of new businesses.

Column 3

PAN-based and pitch-based carbon fibers

There are two types of carbon fibers: PAN-based carbon fibers derived from acrylic fibers and pitch-based carbon fibers derived from pitch, a by-product of petroleum refining. PAN-based carbon fibers constitute approximately 90% of the carbon-fiber market. At present, rayon-based carbon fibers are rarely used.

The growth of pitch-based carbon fibers started in 1963 with the development by Professor Sugio Otani at Gunma University. Pitch-based carbon fibers are classified into optical isotropic pitch type and optical anisotropic pitch type (mesophase pitch type) fibers based on their optical properties. Each type is synthesized by a different method. The pitch-based carbon fibers are produced by refining a starting material, heating and melting the obtained material and extruding the material from a spinneret having numerous holes.

Heating pitch-based carbon fibers in air generates oxidized fibers that do not fuse, even at high temperatures. Heating these fibers in the absence of oxygen generates carbon fibers. Pitch-based carbon fibers with low and high elastic moduli can be produced by altering the synthesis conditions. High-modulus carbon fibers (graphitized fibers) are synthesized by the heat treatment of an anisotropic pitch in the absence of oxygen. Comparatively speaking, the PAN-based carbon fibers are characterized by high strength, and the pitch-based carbon fibers are characterized by high elastic modulus, and they are used for different applications

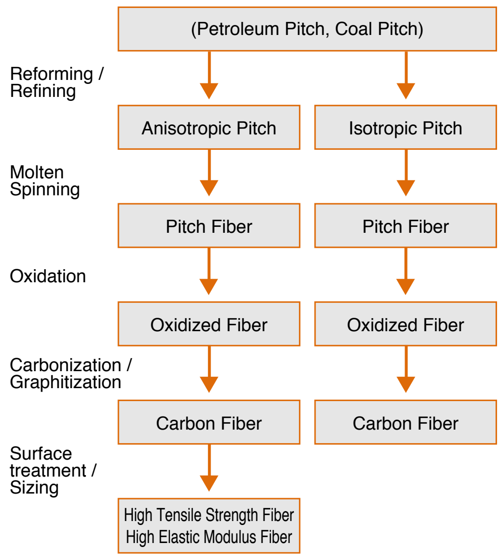


Fig. 7: Manufacturing process of pitch-based carbon fibers
(Source: Japan Carbon Fiber Manufacturers Association)

Column 4

Reason why carbon fibers are lightweight and strong

Carbon fibers exhibit a crystalline-graphite structure. Graphite crystals contain flat laminated sheets that comprise condensed hexagonal benzene rings with a planar hexagonal shape composed of six carbon atoms. Carbon atoms in the flat sheets are bonded to each other by strong covalent bonds (σ and π bonds). Therefore, the sheets exhibit high strength in the planar direction. However, the flat sheets are bonded to each other by van der Waals forces, which are significantly weaker than covalent bonds. Therefore, the gaps between consecutive sheets is large, which are easily delaminated. Carbon fibers are strong because the direction of the flat sheets matches the direction of carbon fibers.

Electrons composing the π-bond between carbons can move within the sheets (delocalization) and act like metal free electrons to create conductivity.

Carbon fibers are lighter than metallic materials because the atomic weight of carbon is lower than that of metals. Moreover, carbon fibers exhibit low density owing to the large gaps between crystalline-graphite flat sheets in the structure of carbon fibers.

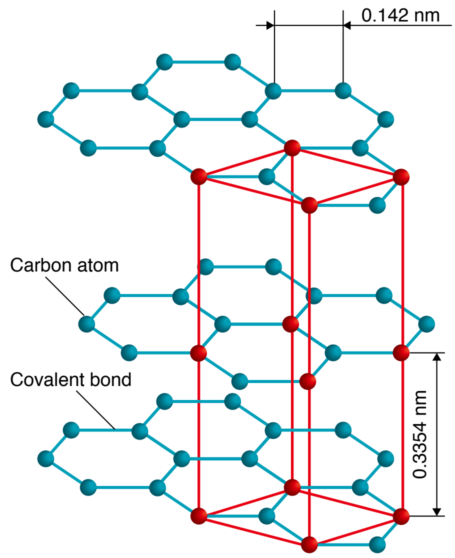


Fig. 8: Crystal structure of graphite

In more details

Fabrication of PAN-based carbon fibers

PAN-based carbon fibers are manufactured using the following steps (products with different qualities can be manufactured by changing the treatment conditions at each step):

❶ **Synthesis of PAN fibers:**

Acrylonitrile is dissolved in a solvent, a polymerization catalyst is added thereto and the mixture is heated to obtain polymer polyacrylonitrile (PAN)*3.

In the spinning step, PAN is extruded from a spinneret with numerous holes into a fibrous shape, washed with water, subjected to primary stretching, oil-agent adhesion, and drying, and finally subjected to secondary stretching.

❷ **Oxidization:**

Reactive distillation (RD) involves reactions, distillation, and separation within a single device (simultaneously).

Typically, the production of chemical substances requires several steps.

In this system, instead of using a reaction vessel, chemical reactions and distillation are carried out inside a distillation device. This improves the reaction efficiency and saves energy.

❸ **Carbonization:**

Heating is carried out in an inert gas (such as nitrogen) within 1,000–2,000°C.

The ladder-shaped molecules formed in the previous step react with each other to release nitrogen and transform into a sheet-shape graphite-network structure partially containing nitrogen atoms, thereby forming carbon fibers with a carbon-atom composition of 90% (or more).

The release of nitrogen and hydrogen atoms from the fibers as gaseous compounds reduces the weight of the fiber per unit length.

❹ **Graphitization:**

Heating is carried out in an inert gas (such as nitrogen) within 2,000–3,000°C.

High-modulus carbon fibers are produced via graphitization.

This step is not included in the production of general purpose carbon fibers that are not intended to have a high elastic modulus.

The degree of graphitization varies with the treatment temperature. Increasing the treatment temperature during graphitization decreases the strength and increases the elastic modulus of the fibers formed.

Carbon fibers graphitized by high-temperature heat treatment are labeled graphite fibers, and can be distinguished from general-purpose carbon fibers.

❺ **Surface treatment/ Sizing:**

Various techniques are used. Generally, electrolytic oxidation is carried out in an electrolyte solution in most cases.

Furthermore, treating the surface with a coating agent (sizing agent) or the like to improve handleability in subsequent processing steps is called sizing.

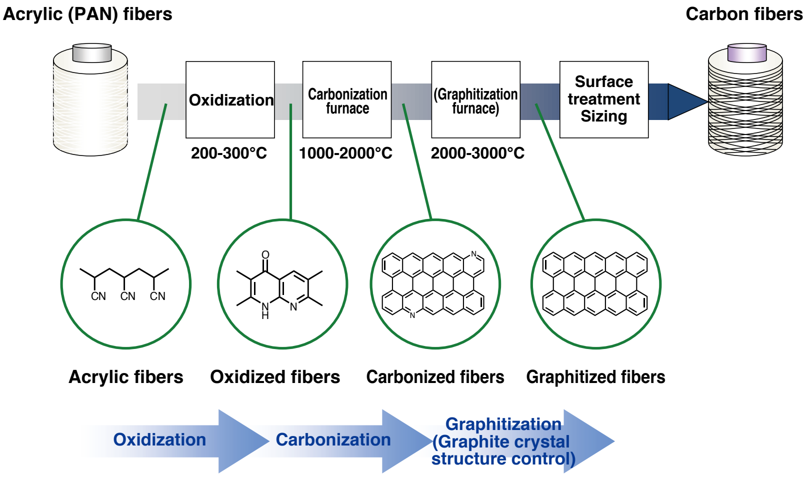


Fig. 9: Manufacturing process of PAN-based carbon fibers

Questions

For deeper understanding

Through this case study, discuss the following questions from the viewpoint of GSC (Green and Sustainable Chemistry).

Q1 Discuss which of the GSC cases best applies to the technologies and products of this teaching material, along with the reasons.

Q2 Implementation in society is vital for any technology to meet the goals of GSC. This involves the simultaneous fulfillment of coexistence with the global environment, the satisfaction of society's needs, and economic rationality.
In the examples of technologies and products in this teaching material, summarize what measures have been taken to meet not only environmental and social satisfaction but also economic rationality.

Q3 In this case study, approaches spanning about half a century were described, from the seed of technology to industrialization with expectations for expansion into a wide range of markets.
Summarize what kind of collaborations were made for this success.

Q4 Describe some reasons for selecting polyacrylonitrile as the raw synthetic fiber in this technology.

Q5 Describe some fields in which carbon-fiber and carbon materials are used (apart from aviation).

Q6 In the periodic table, Si is positioned below carbon. Please describe some similarities and differences between carbon and Si. Please provide some examples of silicon materials.

Introduction of literature

Helpful materials

1) Akio Shindo, CHEMISTRY, 65 (1), 22 (2010)
2) D. Hull and T.W. Cline (translated by Hiroo Miyairi, Kozo Ikegami, Isao Kinpara) "An Introduction to Composite Materials (revised)" (BAIFUKAN CO., LTD.)
3) Sugio Otani, Kensuke Okuda, Shigeru Matsuda "Carbon Fiber" (Tanso Senni in Japanese) (Kindai Henshu Sha)
4) Kenichi Morita, "Carbon Fiber: Theory and Application" (Kindai Henshu Sha) Mitsuhiro Shibata, "Basic Polymer Chemistry" (Kihon Kobunshi Kagaku in Japanese) (Sankyo Shuppan Co., Ltd.)
5) Akihiko Kitano, "CHEMISTRY & EDUCATION," 59 (4), 226 (2011)
6) Nobuyuki Odagiri, "Journal of the Japan Society for Composite Materials," 21, (4), 152 (1995) Committee of The Japan Carbon Fiber Manufacturers Association (JCMA), Japan Chemical Fibers Association (JCFA) http://www.carbonfiber.gr.jp/

"The Statement 2015" declaring global partnership towards implementing GSC was adopted at the 7th International GSC Conference (GSC-7) held in 2015, 12 years after the previous Conference in Tokyo.

(See JACI Website: http://www.jaci.or.jp /images/The_statemant_2015_final_20151118.pdf)

The Statement 2015

We, the participants of the 7th International GSC Conference Tokyo（GSC-7）and 4th JACI/GSC Symposium make the following declaration to promote “Green and Sustainable Chemistry（GSC）” as a key initiative in the ongoing efforts to achieve global sustainable development.

The global chemistry community has been addressing future-oriented research, innovation, education, and development towards environmentally-benign systems, processes, and products for the sustainable development of society.

In response to the Rio Declaration at the Earth Summit in 1992 and subsequent global Declarations, the global chemistry community has been working on challenges in a unified manner linking academia, industry, and government with a common focus to advance the adoption and uptake of Green and Sustainable Chemistry. The outcomes include the pursuance of co-existence with the global environment, the satisfaction of society’s needs, and economic rationality. These goals should be pursued with consideration for improved quality, performance, and job creation as well as health, safety, the environment across the life cycles of chemical products, their design, selection of raw materials, processing, use, recycling, and final disposal towards a Circular Economy.

Long-term global issues, in areas such as food and water security of supply, energy generation and consumption, resource efficiency, emerging markets, and technological advances and responsible industrial practices have increasingly become major and complicated societal concerns requiring serious attention and innovative solutions within a tight timeline. Therefore, expectations are growing for innovations, based on the chemical sciences and technologies, as driving forces to solve such issues and to achieve the sustainable development of society with enhanced quality of life and well-being.

These significant global issues will best be addressed through promotion of the interdisciplinary understanding of Green and Sustainable Chemistry throughout the discussion of “ Toward New Developments in GSC. ”

The global chemistry community will advance Green and Sustainable Chemistry through global partnership and collaboration and by bridging the boundaries that traditionally separate disciplines, academia, industries, consumers, governments, and nations.

July 8, 2015
Kyohei Takahashi
on behalf of Organizing Committee
Milton Hearn AM, David Constable,
Sir Martyn Poliakoff, Masahiko Matsukata
on behalf of International Advisory Board
of 7th International GSC Conference Tokyo (GSC-7),
Japan July 5-8, 2015

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GSC : Green and Sustainable Chemistry

Chemical sciences and technologies
which are benign to both human health and the environment,
and support the development of a sustainable society.

Introduction to GSC

Learning from social practice cases that received the GSC Awards

Global issues, in areas such as resources and energy, global warming, water and food have increasingly become major and complicated concerns. Innovations for achieving both environmental conservation and economic development are needed in order to resolve these issues and realize the sustainable development of society, and expectations for GSC continue to rise. In this textbook series, technologies and products that have received the GSC Awards given to great achievements contributing to the progress of GSC are explained, so that everyone can understand “what is GSC?” and take responsibility for realizing a sustainable society.

Special Edition

“Introduction to SDGs” Sustainable Development Goals GSC plays a driving role in SDGs

Let's change the world towards a sustainable future!

The SDGs are global goals adopted by the United Nations, and it is essential to harmonize the three elements of economy, society, and the environment in order to achieve sustainable development. This way of thinking is shared with the GSC, which aims to achieve both environmental conservation and economic development for the sustainable development of society. As a special issue, this text aims to explain the SDGs from the perspective of the GSC and encourage everyone to think about and put them into practice.

No.1

New laundry proposal for pioneering a sustainable society

Kao Corporation

The "new laundry proposal for pioneering a sustainable society" of Kao Corporation, which received the Minister of Economy, Trade and Industry Award of the 12th GSC Awards (2012), is characterized by the introduction of Life Cycle Assessment (LCA) into the development of laundry detergents, and the proposal to reduce laundry-related environmental impacts together with consumers by using just one rinse cycle in laundry. How was this innovation generated that simultaneously satisfies environmental friendliness, social contribution and economic rationality?

No.2

Novel Non-phosgene Polycarbonate Production Process Using By-product CO_2 as Starting Material

Asahi Kasei Corporation

The great success of this technology is that unlike the conventional polycarbonate production process, it does not use toxic phosgene as a starting material. At the same time, the technology was revolutionary because it achieved saving of both resources and energy. More than 10 years have passed, and the technology has been widely commercialized all over the world. This worldwide use was highly regarded, and the process became the first technology by a Japanese company to receive the Heroes of Chemistry Award from the American Chemical Society in 2014. What kind of technology is involved in this world-renowned polycarbonate production process?

No.3

Development of Carbon Fiber Composite Materials for Lightweight Commercial Airplanes

Toray Industries, Inc.

TORAY's carbon fiber reinforced plastic developed through over 40 years of research and development has features of high toughness (material tenacity) in combination with light weight and flexibility. The high toughness carbon fiber reinforced plastic (high toughness CFRP) realizes weight reduction of airplanes which is effective in improving fuel consumption, and makes a substantial contribution to reducing environmental impact.

No.4

Development and Commercialization of High Performance Transparent Plastics Derived from Plant-Based Raw Material

Mitsubishi Chemical Corporation

"DURABIOTM", the transparent engineering plastic made from renewable resources developed by the company, not only contributes to the reduction of environmental impact, but also realizes performance exceeding that of conventional engineering plastics in terms of optical characteristics, weathering resistance, etc.

No.5

Development of High-Performance Reverse Osmosis Membrane Contribution to the solution of global water issues

Toray Industries, Inc.

This reverse osmosis membrane can be used in not only seawater but also river water, sewage wastewater, and various other water treatment systems, providing high quality water while saving energy.

No.6

Development of Low Environmental Load Battery for Idling-Stop System Vehicle with High Charge Acceptance and High Durability

Hitachi Chemical Co., Ltd.
(Currently Energywith Co., Ltd.)
Hitachi, Ltd.

Idling-stop systems heavily burden on the battery, causing existing batteries to rapidly degrade, with short battery lifetimes. This technology resolves this problem and contributes to the reduction in CO_2 emissions.

No.7

Development of Water-based Inkjet Ink for Food Package

Kao Corporation

Kao Corporation developed a “water-based inkjet ink” for printing on the plastic films used for packaging daily commodities and food.
The ink maintains a high image quality and has lower volatile organic compound emissions, thereby reducing its environmental impact.

No.8

Development and Commercialization of a New Manufacturing Process for Propylene Oxide Utilizing Cumene Recycling

Sumitomo Chemical Co., Ltd.

Sumitomo Chemical Co., Ltd. developed a new manufacturing process for propylene oxide, which is used as a raw material for polyurethane and other materials.
The new process enables high yields of propylene oxide while reducing its environmental impact.

You can read them in “PDF” and “HTML” that is easy to read on mobile phones.

Please take a look!

https://www.jaci.or.jp/english/gscn/GSCgs/spmenu/page_19_01_sp.php

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