High Performance Carbon Fibers

September 17, 2003

A National Historic Chemical Landmark

AMERICAN CHEMICAL SOCIETY

SCIENCE THAT MATTERS

“The full history of carbon fibers has yet to be written: the industry is barely out of its infancy.”

—Roger Bacon and Charles T. Moses, *Carbon Fibers, From Light Bulbs to Outer Space*

carbon

Celebrating Chemistry

The American Chemical Society designated the development of high performance carbon fibers at Union Carbide in Parma, Ohio, a National Historic Chemical Landmark on September 17, 2003. For additional information see our Web site: www.chemistry.org/landmarks.

Bacon’s Breakthrough

The modern era of carbon fibers began in 1956, when Union Carbide, now part of GrafTech International, opened its Parma Technical Center just outside Cleveland. The complex was one of the major laboratories of Union Carbide’s basic research program, modeled after the university-style corporate laboratories that became popular in the late 40s and 50s. These facilities gathered young, bright scientists from a variety of backgrounds and let them loose on their favorite projects, giving them an extraordinary degree of autonomy.

With a freshly minted Ph.D. in physics, Roger Bacon joined the Parma staff in 1956. “I got into carbon arc work, studying the melting of graphite under high temperature and pressures,” Bacon recalls*. The equipment was akin to the early carbon arc streetlamps, only operating at much higher pressures. Small amounts of vaporized carbon would travel across the arc and then deposit as liquid. As Bacon decreased the pressure in the arc, he noticed that the carbon would go straight from the vapor phase to the solid phase, forming a stalagmite-like deposit on the lower electrode.

The year was 1958, and Bacon had demonstrated the first high-performance carbon fibers. In fibrous forms, carbon and graphite are the strongest and stiffest materials for their weight that have ever been produced. Bacon demonstrated fibers with a tensile strength of 20 Gigapascals (GPa) and Young’s modulus of 700 GPa. Tensile strength measures the amount of force with which a fiber can be pulled before it breaks; Young’s modulus is a measure of a material’s stiffness, or its ability to resist elongation under load. For comparison, steel commonly has a tensile strength of 1-2 GPa and Young’s modulus of 200 GPa.

“After studying the heck out of these things, I finally published a paper in the *Journal of Applied Physics* in 1960,” Bacon says. The paper has since become a milestone, partially because some have claimed that Bacon may have been the first person to produce carbon nanotubes — hollow cylinders of graphite with diameters on the order of single molecules. Their incredible properties have made nanotubes one of the hottest areas of research in recent years, promising to revolutionize just about every area of science. “I may have *made* nanotubes, but I didn’t discover them,” he says.

Bacon’s fibers were still just a laboratory phenomenon, not a practical development. “I estimated the cost of what it took to make them, and it was $10 million per pound,” he says. To tap their full potential, manufacturers needed a cheap and efficient way to produce the fibers. Much of the research in the ensuing decades was dedicated to exactly that.

Flexible fibers from rayon

As early as 1959 — just one year after Bacon’s discovery — scientists at Parma had taken a step toward producing high-performance carbon fibers. Curry Ford and Charles Mitchell patented a process for making fibers and cloths by heat-treating rayon to high temperatures, up to 3,000 ºC. They had produced the strongest commercial carbon fibers to date, which led to the entry of carbon fibers into the “advanced composites” industry in 1963.

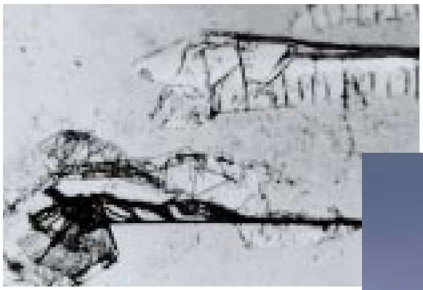
The first truly high-modulus commercial carbon fibers were invented in 1964, when Bacon and Wesley Schalamon made fibers from rayon using a new “hot-stretching” process. They stretched the carbon yarn at high temperatures (more than 2800 ºC), orienting the graphite layers to lie nearly parallel with the fiber axis. The key was to stretch the fiber during heat up, rather than after it had already reached high temperature. The process resulted in a tenfold increase in Young’s modulus — a major step on the way to duplicating the properties of Bacon’s graphite whiskers.

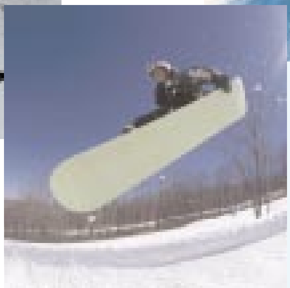
Union Carbide developed a series of high-modulus yarns based on the hot-stretching process, beginning in late 1965 with “Thornel 25.” The trade name was derived from Thor, the Norse god for strength, and the Young’s modulus of the fibers — 25 million pounds per square inch (psi), which is equivalent to about 172 GPa. The Thornel line continued with increasingly higher levels of modulus for more than ten years.

Polyacrylonitrile: A concurrent development

While researchers in the United States were reveling in rayon, scientists overseas were busy creating their own carbon fiber industries based on polyacrylonitrile, or PAN, which had been passed over by U.S. producers after unsuccessful attempts at making high-modulus fibers.

PAN-based fibers eventually supplanted most rayon-based fibers, and they still dominate the world market. In addition to high-modulus fibers, British researchers in the mid-1960s also developed a low-modulus





fiber from PAN that had extremely high tensile strength. This product became widely popular in sporting goods such as golf clubs, tennis rackets, fishing rods, and skis; it is also extensively used for military and commercial aircraft.

Singer's taffy pull

Leonard Singer came to Parma in the mid-1950s with little experience in carbon or graphite. He was attracted to the "utopian flavor" of the place, and he planned to continue his work with electron paramagnetic resonance. He was using this research technique to study the underlying mechanism of carbonization, which involved heating various petroleum- and coal-based materials. Heating organic substances like these inevitably leads to the formation of a pitch — a tar-like mixture of hundreds of branched compounds with different molecular weights. Pitch is an important high-carbon organic precursor used in the manufacture of a number of carbons and graphites.

Two Australian scientists had recently made an important discovery involving pitches. Most pitches are isotropic, having identical properties in all directions, but these researchers showed how a pitch can be polymerized slightly further to orient the molecules in a layered form. "This happens because of the existence of a liquid crystal state, which is also called a mesophase," Singer says. "That really solved the orientation mystery which had been bothering me for a long time."

In 1970 Singer and his assistant, Allen Cherry, designed a "taffy-pulling" machine that applied stress to the viscous mesophase to align the molecules, and then heated the material to convert it to a highly oriented carbon fiber. The process worked, and subsequent analyses verified that they had highly-oriented graphitizable carbon fibers.

The physical properties of these graphitized mesophase pitch fibers were astounding. Not only did they have an ultra-high elastic modulus, approaching 1,000 GPa, but these were also the first carbon fibers with ultra-high thermal conductivity. This made them especially useful for any application where stiffness and heat removal were important — such as aircraft brakes and electronic circuits. Most mesophase pitch-based fibers did not achieve the high tensile strengths of some PAN and rayon fibers, except in the laboratory.

Pitch is a fairly inexpensive raw material. However, depending on the form and properties of the desired product, the cost of the final product, mat, strands, or cloth, can vary widely. On the one hand, the mesophase pitch-based carbon fibers used in aircraft brakes and reinforced concrete are relatively inexpensive. On the other hand, due to the extremely high graphitizing temperatures required, the ultra-high modulus, high thermal conductivity fibers required in satellites and other spacecraft can be expensive.

Carbon fibers today

All commercial carbon fibers produced today are based on rayon, PAN, or pitch. Rayon-based fibers were the first in commercial production in 1959, and they led the way to the earliest applications, which were primarily military. Fibers from PAN fueled the explosive growth of the carbon fiber industry since 1970, and they are now used in a wide array of applications such as aircraft brakes, space structures, military and commercial planes, lithium batteries, sporting goods, and structural reinforcement in construction materials. Pitch-based fibers are unique in their ability to achieve ultra-high Young's modulus and thermal conductivity and, therefore, have found an assured place in critical military and space applications. But their high cost has kept production to a minimum; a lower modulus, non-graphitized mesophase pitch-based fiber, which is much lower in cost, is used extensively for aircraft brakes.

The cost of making carbon fibers has been reduced drastically in the last 20 years, and researchers are bringing that cost down every day. As they do, many of the applications once considered impossible will become reality. Carbon fibers are used sparingly in automotive applications, but some day entire body panels may be made from them. All high-speed aircraft have carbon fiber composites in their brakes and other critical parts, and in many aircraft they are used as the primary structures and skins for entire planes. Carbon fibers could even be used to develop earthquake-proof buildings and bridges.

National Historic Chemical Landmark

The American Chemical Society designated the development of high performance carbon fibers at Union Carbide in Parma, Ohio, as a National Historic Chemical Landmark on September 17, 2003. The plaque commemorating the event reads:

Scientists at the Parma Technical Center of Union Carbide Corporation (now GrafTech International) performed pioneering research on carbon fibers, for their weight the strongest and stiffest material known at the present time. In 1958 Roger Bacon demonstrated the ultrahigh strength of graphite in a filamentary form. Seven years later continuously processed high performance carbon yarn, from a rayon precursor, was commercialized. In 1970 Leonard Singer produced truly graphitic fibers, leading to the commercialization of carbon yarn derived from liquid crystalline pitch. Carbon fibers are used in aerospace and sports applications.

About the National Historic Chemical Landmarks Program

The American Chemical Society, the world's largest scientific society with more than 161,000 members, has designated landmarks in the history of chemistry for more than a decade. The process begins at the local level. Members identify milestones in their cities or regions, document their importance, and nominate them for landmark designation. An international committee of chemists, chemical engineers, museum curators, and historians evaluates each nomination. For more information, please call the Office of Communications at 202-872-6274 or 800-227-5558, e-mail us at nhclp@acs.org, or visit our web site: www.chemistry.org/landmarks.

A nonprofit organization, the American Chemical Society publishes scientific journals and databases, convenes major research conferences, and provides educational, science policy, and career programs in chemistry. Its main offices are in Washington, DC, and Columbus, Ohio.

Acknowledgments:
Photo Credit: Union Carbide Corporation, Pharma Technical Center

Written by Jason Gorss

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