
**High-Performance Structural Fibers for Advanced Polymer Matrix Composites**

Committee on High-Performance Structural Fibers for Advanced Polymer Matrix Composites, National Research Council

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Committee on High-Performance Structural Fibers for Advanced Polymer Matrix Composites
National Materials Advisory Board
Division on Engineering and Physical Sciences

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# Preface

A high-performance polymer matrix composite (PMC) consists of a thermoset or thermoplastic resin matrix reinforced by fibers that are much stronger and stiffer than the matrix.[1] Structural fibers that may be used as the reinforcement phase include carbon, aramid, glass, and many others. PMCs are attractive because they are lighter, stronger, and stiffer than conventional materials, with the additional advantage that their properties and form can be tailored to meet the needs of a specific application. Depending on the characteristics of the resin matrix and fiber reinforcements, PMCs may also be tailored to exhibit such properties as high thermal or electrical conductivity, stealth characteristics, and sensor capabilities.

High-performance PMCs were initially developed in the 1960s and 1970s for use in military applications such as aerospace and missile systems. The results may be seen today in systems fielded by each of the military services. For example, the U.S. Navy's F/A-18 E/F consists of 19 percent carbon-epoxy composites by weight, and the forthcoming Joint Strike Fighter could be between 25 and 30 percent composite by weight. The Army has used composites extensively in munitions, ground vehicles, and soldier protection systems. The Army's M829A2 antitank weapon employs a composite sabot that accounts for 385,000 pounds of composite per year, making it the largest single user of carbon-epoxy in the Department of Defense (DoD).[2]

As the prices of high-performance fibers declined in the 1980s due to process improvements, composites began to find applications in commercial aircraft, in industrial applications such as pressure vessels, and in sports and leisure equipment. Today, these commercial markets have expanded to such an extent that DoD accounts for less than 10 percent of the domestic market and less than 5 percent of the world market.[3] The relative decline in percentage of the DoD demand for composites compared with commercial market demand has important implications for future DoD access to affordable fibers having properties to meet its specifications.

Composites are expected to play an even greater role in military systems of the future. The Army's Objective Force, part of DoD's Future Combat System, exemplifies an ongoing transformation to an entirely new future combat system incorporating advanced materials and design concepts for munitions, armament, and hull structures that will be light enough to be deployed rapidly on C-130 aircraft.[4] Ground vehicles will be needed in the 10- to 20-ton range with superior mobility, transportability, survivability, and lethality for a variety of missions. In the Army, a 100-fold increase in composites usage is projected to

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1 R.B. Aronson. 1999. Machining composites. Manufacturing Engineering 122:52-58.

2 B.K. Fink. 1998. Army requirements for high-performance structural fibers for advanced polymer matrix composites. Briefing to this study committee on September 9.

3 Intertech. 2004. The Global Outlook for Carbon Fiber. Proceedings of a conference in Hamburg, Germany, October 18-20. Portland, Me.: Intertech Corporation.

4 National Research Council. 2003. The Use of Lightweight Materials for Army Trucks. Washington, D.C.: National Academies Press.

satisfy weight and performance requirements.[5] Although a 100-fold increase in the Army's currently small usage may not revolutionize the industry, even more extensive use is expected in Navy and Air Force systems. For example, the deckhouse structure for the Navy's new DD(X)[6] is constructed of a carbon-fiber-reinforced vinyl ester with a balsa core. The total weight for one ship deckhouse is 500 tons of structure. The Navy currently plans on producing one to two per year with the composite deckhouse for a total of 20 to 32 ships.[7]

As future military systems rely more heavily on composite materials in their transformation to become lighter, faster, and more lethal, the military will continue to require access to reliable sources of affordable, high-performance fibers and, where possible, will seek to take greater advantage of commercial off-the-shelf materials and manufacturing processes. Although specialty fibers are available that appear to meet DoD's current performance requirements, fiber costs over the next 10 years for defense applications could be significantly reduced if DoD accepts commercially available fibers. If strict specification and qualification requirements can be reduced or modified, commercially available fibers and composites may meet many DoD needs. It is also likely that applications 10 to 20 years in the future for armor and spacecraft, for example, will require improved fibers and composites.

As a result of this general speculation, in 1998 the Office of Defense Research and Engineering in the Department of Defense requested that the National Research Council (NRC) undertake a study of the challenges and opportunities associated with advanced composite materials, with emphasis on high-performance fibers. The appointed committee undertook the following tasks:

- Identify technological trends in the fiber industry including improved mechanical properties, low-cost process technology, and manufacturing controls.
- Identify market and business trends in the carbon and high-performance organic fiber industries, including consumption volume, production capacity, and historical and projected prices as a function of product form (e.g., tow count or the number of parallel and uncut filaments in a fiber bundle) and properties.
- Characterize the current state of the carbon and high-performance organic fiber manufacturing industries, both domestic and worldwide, and assess the capabilities and application priorities of fiber suppliers.
- Identify probable future DoD applications of organic-matrix composites, considering performance, availability, composite processing and component design, and cost drivers. Particular attention will be placed on the relationships between cost and availability and cost and performance.
- Suggest opportunities for DoD-sponsored research to advance structural fiber technologies, including those involving manufacturing process and control technologies. Means to reduce product costs of fibers and composites will be emphasized.
- Suggest mechanisms for DoD to take advantage of low-cost processing and composite manufacturing innovations associated with lower-cost, higher-volume commercial applications while maintaining fiber performance, product consistency, and traceability.

The Committee on High-Performance Structural Fibers for Advanced Polymer Matrix Composites conducted an extended study of the topic, and the duration of the effort spanned a number of important changes in the fiber industry. The main focus of this document is on carbon fibers and high-performance organic fibers. Because commodity fibers—those with lower specific properties, such as glass fibers—

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5 B.K. Fink. 1998. Army requirements for high-performance structural fibers for advanced polymer matrix composites. Briefing to this study committee. September 9.

6 The Navy's new DD(X) program is the centerpiece of a family of three surface combatant ships, including a destroyer, a cruiser, and a smaller craft for littoral operations. The cruiser and destroyer are expected to share a common hull design. The littoral combat ship will most likely have an advanced hull designed for high speed and a shallow draft, and with a composite deckhouse.

7 G. Camponeschi. 2004. Panel briefing to the Society for the Advancement of Materials and Process Engineering conference, May 18.

are not as relevant to future military systems, they are not discussed here. However, these lower-performance fibers dominate the commercial PMC market volume. For example, in 2003 the world market for carbon fiber was approximately 38 million pounds, whereas the world market for glass fiber was more than 100 times greater, approximately 5 billion pounds.[8]

Although the main emphasis of this study is on high-performance fibers, the committee felt it impossible to discuss the cost and performance of advanced PMCs by focusing on fibers alone; polymer matrix materials must also be considered, as well as the interface connecting the fibers to the matrix and the processing path. The characteristics of the matrix and fiber-matrix interface strongly influence the available manufacturing processes and the final properties of the PMC; therefore, these topics are also discussed here, albeit in somewhat less detail than fibers.

The committee was tasked with suggesting opportunities for DoD-sponsored research to advance structural fiber technologies. Historical experience shows that the time required for development of a new fiber, its associated manufacturing processes, testing, and incorporation into a functional composite structure is generally measured in decades. Thus, new fibers developed today are not likely to find practical application in the production of DoD systems in the next 5 to 10 years. The committee therefore divided its discussion of research and development opportunities discussion into two parts: opportunities to take advantage of existing fibers (next 5 to 10 years) and opportunities to develop new fibers and applications (beyond the next 10 years).

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the National Research Council's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report: D. Bruce Chase, E.I. du Pont de Nemours & Company; D.J. DeLong, DeLong and Associates; Gail Hahn, The Boeing Company; James B. O'Dwyer, PPG Industries; R. Byron Pipes, Purdue University; Steve Russell, Aldila Carbon Fiber Technology LLC; and James Seferis, University of Washington.

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations, nor did they see the final draft of the report before its release. The review of this report was overseen by Eli M. Pearce, Polytechnic University. Appointed by the National Research Council, he was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the institution.

The committee acknowledges speakers from government and from industry who took the time to share their ideas and experiences. The following former committee members also greatly assisted the work of the current committee through their participation in many of its activities: John C. Adelmann, Sikorsky Aircraft Corporation; Lynn W. Jelinski, Sunshine Consultants, Inc.; James E. McGrath, Virginia Polytechnic Institute and State University; Paul D. Palmer, Thermo Fibergen; and George S. Springer, Stanford University. Finally, the committee acknowledges the contributions to the completion of this report from the staff of the National Academies, including Charles T. Hach, Julius C. Chang, Greg Eyring, and Bonnie Scarborough.

John W. Gillespie, Jr., *Chair*
Committee on High-Performance Structural Fibers
for Advanced Polymer Matrix Composites

[8] Fiber Organon. 2004. U.S. Manufactured Fiber Capacity, Production & Utilization Review. January, p. 7.

# Contents

# Executive Summary

A polymer matrix composite (PMC) consists of a thermoset or thermoplastic resin matrix reinforced by fibers that are much stronger and stiffer than the matrix. PMCs are attractive because they are lighter, stronger, and stiffer than unreinforced polymers or conventional metals, with the additional advantage that their properties and form can be tailored to meet the needs of a specific application. High-performance fiber reinforcements are of the highest interest for military and aerospace composite applications; these include carbon fibers and such organic fibers as aramids, liquid crystalline polymers, and ultrahigh-molecular-weight polyethylene.[1]

When high-performance carbon fibers were first developed in the 1960s, their high cost (as much as $400 to $500 per pound) limited their applications to high-value military aerospace and space systems. The results of early military composite development programs can be seen today in systems fielded by each of the military services. For example, more than 350 parts of the F-22 Raptor, accounting for 25 percent of the structural weight, are carbon-epoxy composites.[2] Further, the developmental Joint Strike Fighter will be between 25 and 30 percent composite by weight. The Army now uses carbon-thermoplastic composites in high volume production of sabots for the M829A3 munition.

Composites are expected to play an even greater role in military systems of the future. The Army's Objective Force, part of the Defense Department's (DoD's) Future Combat System, exemplifies an ongoing transformation to an entirely new future combat system incorporating advanced materials and design concepts for munitions, armaments, and hull structures for manned and unmanned robotic vehicles that will be light enough to be rapidly deployed on C-130 aircraft. Ground vehicles in the Future Combat System will have to weigh between 10 and 20 tons and have superior mobility, transportability, survivability, and lethality for a variety of missions. The Navy is considering carbon fiber composites for next-generation topside ship structures such as destroyers, aircraft carriers, littoral combat ships, and other high-speed vehicles to satisfy the weight and performance requirements of these systems. These applications represent a possible 100-fold increase in carbon fiber usage.

High-performance organic fibers are used extensively in soldier protection systems ranging from body armor and helmets to spall liners in ground vehicles. The global war on terrorism has increased the demand for these fibers for crew protection kits and for tactical vehicles for immediate deployment, as well as for replacement components needed by forces in the field. The new M5® fiber, being developed with improved compressive properties, may enable improved structural armor applications.[3]

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[1] The properties of composite structures depend not only on the fiber reinforcements, but also on the polymer matrix, the characteristics of the interface between the fiber and matrix, and the manufacturing process used to form the finished structure.

[2] Composites are commonly denoted by their fiber-matrix composition. A carbon-epoxy composite will consist of carbon fibers in an epoxy matrix.

[3] M5® is a registered trade name for poly{2,6-diimidazo[4,5-b:4',5'-E]pyridinylene-1,4-(2,5-dihydroxy)phenylene}. The fiber was engineered over a 10-year period by a team of scientists led by Doetze Sikkema while working for Akzo Nobel, a pharmaceuticals, coatings, and chemical company headquartered in the Netherlands. The design

## DEVELOPMENT OF HIGH-PERFORMANCE FIBERS

The development pathways of high-performance carbon and organic fibers have been driven by decidedly different cost and performance requirements. These different pathways strongly affect the future prospects for military and commercial applications of these fibers.

### *High-Performance Carbon Fibers*

Carbon fibers are typically produced by spinning and then thermally carbonizing one of three types of precursor fibers: polyacrylonitrile (PAN), pitch, or rayon. Depending on the type of precursor and the processing method, the finished carbon fiber will have a different microstructure and therefore different properties. PAN-based fibers have a disordered microstructure that typically confers higher tensile and compressive strengths, while pitch-based fibers have a more crystalline microstructure that results in a higher tensile modulus and much higher (100 times) thermal conductivity. In general, PAN-based fibers dominate applications where strength is critical, and pitch-based fibers dominate applications where heat transfer or stiffness (i.e., more than 80 Mpsi fiber modulus) is important. Around 90 percent of all commercial carbon fibers are produced by the thermal conversion of PAN precursor fibers.[4]

As the carbon fiber industry matured during the 1980s and costs began to decrease, a variety of commercial applications for high-performance composites emerged, including sporting goods, commercial aircraft, and industrial applications. In 2003, the world market demand for PAN-based carbon fiber was approximately 38 million pounds, divided almost equally (10 million to 13 million pounds each) among North America, Europe, and Asia. Aerospace applications predominate in North America, while industrial and aerospace applications are emphasized in Europe, and sports and leisure are the primary applications in Asia.[5]

As a result, DoD usage, which dominated the U.S. requirements in the 1970s and 1980s, became a smaller part of the total market. In 2003, the lowest prices observed for carbon fibers were $5.25 per pound for a standard-modulus (32 Mpsi) fiber and $17 per pound for an intermediate-modulus (42 Mpsi) fiber. The DoD market was just under 10 percent of the total U.S. carbon fiber market and 4 percent of the world carbon fiber market.

Until the late 1980s, special acrylic fiber (SAF) precursor was used for nearly all PAN-based carbon fibers. This precursor fiber is produced in filament bundle (or tow) sizes of 3,000 (3k), 6,000 (6k), and 12,000 (12k) filaments, and is normally supplied on spools without applying a crimp or twist. The majority of current defense applications are based on the performance and consistency of properties provided by these small-tow, SAF-based carbon fibers.

In response to the emergence and projected growth of such commercial carbon fiber markets as sporting goods, construction, and transportation, a sector of the carbon fiber industry has evolved to produce fibers in large volumes at relatively low cost. In one sector, commercially available PAN fibers are used as precursors to produce carbon fibers in large tow counts, having up to 24k filaments. These precursor fibers are normally used in the textile industry and draw on an approximately 5-billion-pound annual market to bring about lower material costs.

Another sector of the fiber supply base has emerged to meet the increasing demand for commercial applications such as Boeing's 7E7 aircraft using SAF fiber precursors. Japanese companies are establishing domestic capacity for both SAF precursor plants and fiber lines. For example, prices for T700 12k and 24k tows of $5.25 per pound, a historic low, were not uncommon in 2003. At this price, they represent a cost-competitive alternative to the large-tow-count textile-based fibers, with performance comparable to that of the current SAF fibers approved for use by DoD. The combination of lower cost potential and equivalent performance makes these fibers very attractive for future DoD systems. Today, there is another shortage of SAF-based carbon fiber and prices have risen, demonstrating that $5.25 is not a sustainable price for SAF aerospace-grade carbon fiber.

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goal set by Dr. Sikkema was to develop a high-strength synthetic fiber that excelled as both a ballistic fabric and a composite material.

[4] Intertech. 2004. The Global Outlook for Carbon Fiber. Proceedings of a conference in Hamburg, Germany, October 18-20. Portland, Me.: Intertech Corporation.

[5] Fiber Organon. 2004. U.S. Manufactured Fiber Capacity, Production & Utilization Review. January, p. 7.

Further, the capacity for carbon fibers is being driven by the high-volume needs of commercial applications. This may offer additional savings to DoD through economies of scale or simply increased competition to provide the best quality at the lowest price. To increase competition, DoD could take initiatives to establish second sources for all carbon fiber applications. In addition, this commercially driven capacity may provide a primary source of carbon fiber that can supply larger quantities if future expansions are fielded. For example, carbon fiber usage for next-generation ship systems such as DD(X) could exceed current domestic capacity. The continued expansion of the carbon fiber commercial market using high-quality SAF precursors should offer a measure of stability in the fiber supply chain in future DoD applications.

All of these methods to produce carbon fibers for DoD have one significant factor in common, which is the cost burden of qualification and subsequent quality and acceptance testing. One straightforward way to reduce cost over the next decade is to modify specifications to reduce the qualification requirements of these advanced fibers.[6]

### *High-Performance Organic Fibers*

The high-performance organic fiber industry began with the commercial introduction of the *meta*-aramid (*m*-aramid) fiber Nomex in the late 1960s. Since that time, several classes of fibers have been commercialized: high-strength *para*-aramid (*p*-aramid) fibers; liquid crystalline polyester (LCP); high-performance polyethylene (PE); ultrahigh-molecular-weight polyethylene (UHMPE); and most recently poly(*p*-phenylene-2,6-benzobisoxazole) (PBO). A new fiber M5 (poly{2,6-diimidazo[4,5-*b*:4',5'-*e*]pyridinylene-1,4-(2,5-dihydroxy)phenylene}), also known as PIPD, is in late development stages with the start-up of a pilot plant expected in 2005.

Like the carbon fiber industry, developments in organic fiber technology during the 1970s and 1980s enabled the use of lightweight polymer-matrix composites in military and commercial applications. Unlike the carbon fiber industry, however, growth in the high-performance organic fiber industry was driven from the beginning by a combination of military and commercial applications and aerospace and non-aerospace applications. The unusual combination of mechanical, thermal, and other properties found in high-performance organic fibers (especially PBO and aramids), as well as the ability to tailor these properties for specific applications, has enabled this wide range of uses.

Demand for high-performance organic fibers such as *p*-aramids and *m*-aramids grew steadily at a rate of 6 to 7 percent from the late 1970s to the mid-1990s, due to the large number of commercial applications. These two fiber types represent more than 90 percent of worldwide demand for high-performance organic fibers and can therefore be used as a good approximation of general consumption trends. By 2002, demand for *p*-aramid alone had risen to approximately 90 million pounds, approximately three times the demand for PAN-based carbon fiber. In the mid-1990s, substantial production capacity existed for high-performance organic fibers in the United States, Europe, and Japan.

The high-performance organic fiber industry has grown steadily in recent decades and is stable. From the beginning, the industry's dependence on high-volume commercial applications, rather than DoD applications, has contributed to its stability. Demand for high-performance organic fibers remains high as a result of their broad range of applications, and there is potential for future growth. During the past 4 to 5 years there has been significant investment in capacity for *p*-aramids and polyethylene fibers. While there may be room for limited capacity expansion, in the next 5 to 10 years there will be a need for additional capacity requiring a significant investment that will include ingredients and polymer and fiber production facilities. Although DoD represents only a small portion of the overall market, the specificity of DoD requirements may focus attention on issues of supply.

## FINDINGS AND CONCLUSIONS

### *Fiber Supply*

The 2004 worldwide capacity of carbon fibers (SAF based and textile precursor based) was expected to be more than 70 million pounds. Consumption was expected to be more than 40 million

[6] National Research Council. 2004. Accelerating Technology Transition. Washington, D.C.: National Academies Press.

pounds and increasing.[7] In this changing market, it appears that each carbon fiber supplier has targeted specific market segments and is building facilities and directing product portfolios to support its chosen strategies. Although some producers have indicated that the high cost of adding new facilities is a barrier to increasing capacity, DuPont, Honeywell, Dyneema, Toho, and Toray are all adding capacity in the United States. This added capacity will help to meet the anticipated shortage of carbon fiber produced with SAF precursor and meet the demand for organic fiber for military and homeland security applications.

Significant investment has been made over the past 4 to 5 years in capacity for *p*-aramid and PE fibers. Some of this capacity has been developed for military products, but most is targeted toward nonmilitary applications. Current expansion is targeted to meet the military needs for soldier protection and homeland security. An important aspect of this continuing investment is an M5 pilot plant start-up planned for 2005. This new M5 capacity will enable ballistic and structural performance evaluation to be conducted on full-scale components.

### *Fiber Demand*

As the fiber industry matured during the 1980s and costs began to decrease, a variety of commercial applications for high-performance composites emerged, including sporting goods, commercial aircraft, and various industrial applications. As a result, DoD usage, which dominated U.S. requirements in the 1970s and 1980s, became a smaller part of the total market. In 2003, the historic and unsustainably low prices observed for carbon fibers were $5.25 per pound for a standard-modulus (32 Mpsi) fiber and $17 per pound for an intermediate-modulus (42 Mpsi) fiber. The DoD market was just under 10 percent of the total U.S. market and 4 percent of the world market.

Military usage is a decreasing share of the total U.S. carbon fiber market—from 43 percent in 1989 to 9 percent in 2003. Because the military usage in the total market is ever smaller—currently less than 4 percent of the world market—the installed integrated capacity in North America is adequate to supply all projected DoD needs for the next decade. In addition, the fiber modulus and strength properties of current production meet DoD's performance requirements for the near term. For the suppliers, this increasingly tight market is expected to lead to pricing structures that could support sustainable reinvestment. For the buyers, in cases where DoD relies on a sole source, prices could remain high.

Significant demand from DoD combined with a technological design shift toward lighter-denier products is expected to strain existing capacity for structural organic fibers. Additional military and homeland security applications are also emerging. In particular, the demand for organic fibers is currently high to satisfy the military's need for body armor and crew protection kits for tactical vehicles. This demand is predicted to remain high for 2 years and then decrease gradually.

### *Fiber Technology*

A few companies continue to invest in new carbon fiber technologies. This investment has been primarily in process improvements and better manufacturing controls to decrease variability and reduce cost rather than to improve properties. Because of this trend, any change in carbon fiber properties is expected to be evolutionary, not revolutionary. Any impact of new lower-cost technology is at least 10 years away.

In the organic fiber area, M5 fiber has the potential to become a commercial fiber with a step improvement in functionality, especially to address the need for optimized structural and ballistic properties of interest to DoD. M5 has the potential to meet the future structural and ballistic needs of the Army. Existing fibers, such as Kevlar, have good ballistic properties but poor properties in compression. M5 could be an enabling technology for a new generation of soldier protection systems.

Finally, although significant progress has been made in improving fiber and matrix properties and reducing material costs, similar progress has not been achieved in manufacturing technology and innovative design to lower the cost of composite structures. Composite processing remains a major opportunity for improvement.

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[7] Intertech. 2004. The Global Outlook for Carbon Fiber. Proceedings of a conference in Hamburg, Germany, October 18-20. Portland, Me.: Intertech Corporation.

## CONCLUSIONS AND RECOMMENDATIONS

Accelerating technology transition has been identified as a key target.

- One method to speed new fiber technologies to market, especially for such new fibers as M5® or nanocomposite fibers, would be for DoD to provide a guaranteed initial purchase order if the pilot product meets specified property and price requirements.
- In the near term, DoD should provide significant funding to purchase M5 fiber and rapidly evaluate its properties and applications.

Cost reduction has been identified as a key target.

- A clearly significant way to reduce fiber costs over the next 10 years is to reduce or modify the aerospace specifications and qualification process. The DoD should review existing and new qualifications and material specification documents and reduce testing and quality requirements where possible.
- To reduce acquisition costs, all major DoD programs that use fiber or prepreg should have two qualified sources.
- To reduce manufacturing costs in aircraft structures, DoD should invest in manufacturing technology and innovative design concept development. Promising ways to improve dimensional tolerance and reduce processing variability include investment in new continuous process controls that would contribute to controlling fiber structure and purity, prepreg properties such as fiber weight per unit length, and overall property variability.
- To reduce manufacturing costs across all DoD applications, DoD should initiate a program with university-industry-government participation. Promising manufacturing and design concepts should be assessed, including vacuum-assist resin transfer molding (VARTM) to replace more costly manufacturing processes. Virtual manufacturing and simulation should play an important role in accelerated insertion of materials and processes into DoD systems. Research in automation using simulation, sensing, and control systems should be pursued to advance this process from prototype to a production-ready process.

Improved understanding has been identified as a key target.

- The DoD should take a lead in developing a better design methodology that incorporates variability and stochastic aspects of local properties into lifetime models. DoD personnel should use this improved understanding to develop new design allowables and parameters that prevent overdesign of parts and overspecification of fiber properties.
- The DoD should aid in developing a better understanding of new promising technologies in such areas as micron-scale fibers with nanoscale structure and new sizings with the ability to maximize structural and ballistic properties.

# 1

# High-Performance Fiber Technology

High-performance fibers are those that are engineered for specific uses that require exceptional strength, stiffness, heat resistance, or chemical resistance. There exist a wide variety of fibers with widely ranging properties; Figure 1.1 compares some of the different optimized categories. These fibers have generally higher tenacity[1] and higher modulus[2] than typical fibers. In the larger fiber market, such high-performance fibers are generally niche products, but some are produced in large quantities.

Glass is the oldest high-performance fiber, one that has been manufactured since the 1930s. Today's glass fibers can be found in such end uses as insulation, fire-resistant fabrics, and reinforcement for fiberglass composites such as bathtub enclosures and boats. In addition, continuous filaments of optical-quality glass have revolutionized the communications industry in recent years.

Carbon fiber is one of the most important high-performance fibers for military and aerospace applications. Carbon fiber is engineered for strength and stiffness, but variations differ in electrical conductivity, thermal, and chemical properties. The primary factors governing the physical properties are the degree of carbonization (or the carbon content, usually greater than 92 percent by weight), the orientation of the layered carbon planes, and the degree of crystallization.

Commercial carbon fibers are made by extrusion of some organic precursor material into filaments, followed by a carbonization process to convert the filaments into carbon. Different precursors and carbonization processes are used depending on the desired product properties. Precursor fibers can be specially purified rayon, pitch, or acrylics. The precursor fiber may also be converted into fabric form, which is then carbonized to produce the end product.

High-performance organic fibers have also become very important in recent years. Aramids are among the best known of the high-performance, synthetic, organic fibers. Closely related to the nylons, aramids are polyamides derived from aromatic acids and amines. Because of the stability of the aromatic rings and the added strength of the amide linkages, aramids exhibit higher tensile strength and thermal resistance than the aliphatic polyamides (nylons). The *para*-aramids (*p*-aramids, based on terephthalic acid and *p*-phenylenediamine, or *p*-aminobenzoic acid, exhibit higher strength and thermal resistance than those with linkages in the meta positions of the benzene ring. The greater degree of conjugation and more linear geometry of the para linkages, combined with the greater chain orientation derived from this linearity, are primarily responsible for the increased strength. The high impact resistance of the *para*-aramids makes them popular for “bullet-proof” body armor. For many less demanding applications, aramids may be blended with other fibers.

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[1] Tenacity denotes the relative strength of a textile fiber, expressed in grams of breaking force per denier unit. Denier denotes the system of measuring the weight of a continuous-filament fiber. In the United States, this measurement is used to number all manufactured fibers (both filament and staple) and silk, but excluding glass fiber. The lower the number, the finer is the fiber; the higher the number, the heavier is the fiber. Numerically, a denier is the equivalent to the weight in grams of 9,000 meters of continuous-filament fiber.

[2] Modulus denotes the value of the specific stress (load divided by area) to the strain (such as elongation) of a fiber. It is a measure of the relative flexibility and resilience of a material (i.e., rubber has a low modulus and steel a high one). Modulus is expressed in pounds per square inch.

## CARBON FIBERS

In the 1950s, it was recognized that materials that combine light weight, high strength, and high stiffness are needed to produce ultralightweight structures.[3] Carbon fibers were developed to fill this need. Carbon fibers are typically produced by high-temperature processing of one of three types of precursor fibers: polyacrylonitrile (PAN), pitch, or rayon. Depending upon the type of precursor and processing method, the finished carbon fiber has somewhat different properties. Figure 1.2 compares some of the properties of pitch-based and PAN-based carbon fibers. Typically, PAN-based fibers have a higher specific strength and lower specific modulus than fibers made from pitch or rayon; pitch-based fibers have lower electrical resistivity and higher thermal conductivity. In general, PAN-based fibers are less expensive than pitch-based or rayon-based carbon fibers.

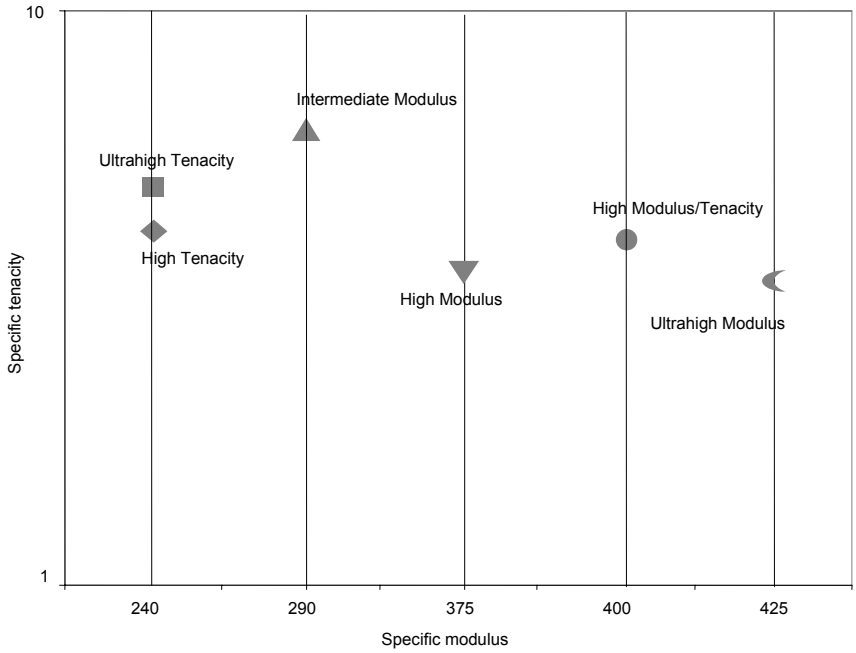


FIGURE 1.1 Relative properties for the different categories of high-performance fibers.

Carbon fibers generally are delivered in "tows," or bundles of fibers. These are found in two forms based on the starting precursor: special acrylic fiber (SAF) or textile tow. Textile tow as referred to here is a modified form of an acrylic fiber used in the textile and carpet industry. The world capacity is around 5 billion pounds. It is made as a large-tow material, with 120k to 320k (k = 1,000) filaments that may be split into smaller tows of around 36k. In most cases, a crimp is applied to allow easier handling of the tow. The textile tow is most often piddled into a box containing 300 to 1,000 pounds for shipping. The crimp is needed to keep the piled fiber together in tows.

The SAF tow, conversely, is manufactured solely for conversion to carbon fiber. It can be a compound similar to a textile tow, but it is made on a special spinning line. The filament count ranges from 3k to 24k or larger if required by a specific manufacturing process, such as pultrusion. This fiber is normally provided on a spool without crimp or twist. The conversion process for the two materials is the same except for the feed end and the take-up end of the line. It is more difficult to maintain a uniform tension on the textile tow precursor, which results in the large tow producing a slightly lower tensile strength and greater variability when compared to SAF materials.

### *PAN-Based Carbon Fiber*

More than 90 percent of all commercial carbon fibers are produced by the thermal conversion of PAN precursor fibers. PAN-based carbon fibers are produced in three distinctly separate process steps: polymerization and wet spinning, stabilization, and carbonization.

[3] E. Fitzer, A. Gkogkidis, and M. Heine. 1984. Carbon fibers and their composites (a review). High Temperatures–High Pressures 16:363-392.

The precursor used to form PAN-based carbon fibers is a binary copolymer of acrylonitrile with 6 to 9 percent of an acid comonomer.[4] Although PAN fibers can be produced by either wet- or dry-spinning processes, wet spinning is used to produce nearly all commercial precursor fibers. The solution used in a wet-spinning process normally consists of from 10 to 30 percent by weight of PAN (or PAN copolymer) dissolved in a polar solvent. This solution is first filtered and then extruded through a thin plate containing thousands of capillaries—termed a spinneret. As the PAN solution is forced through the spinneret capillaries, the shear field tends to orient the solidifying polymeric structure parallel to the direction of flow.

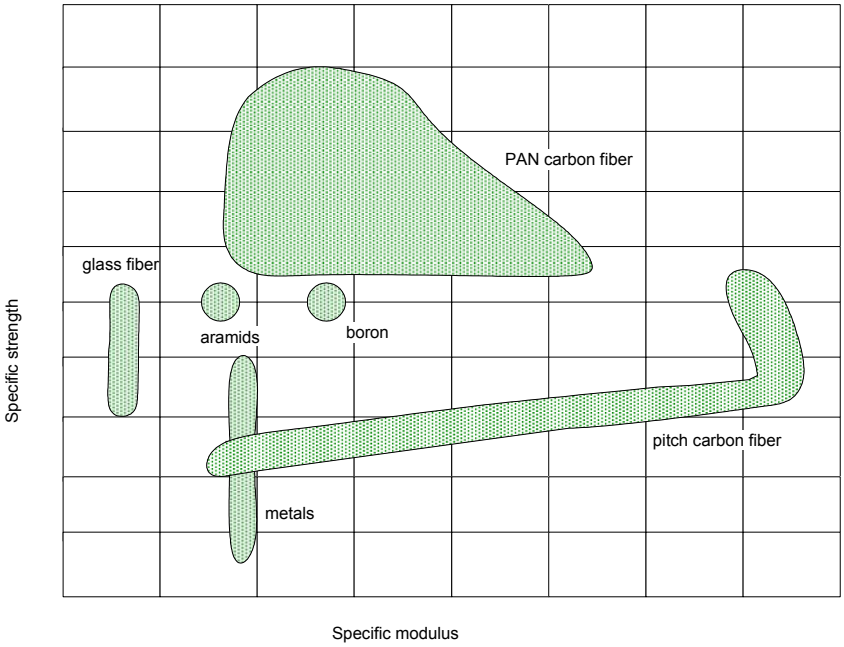


FIGURE 1.2 Generalized specific modulus versus specific strength for several high-performance fibers (carbon, aramid) compared with lower-performing materials (glass, metals). DATA SOURCES: T. Baumeister, 1985. Marks' Standard Handbook for Mechanical Engineers, 8th Edition; J.E. Shigley, 1977, Mechanical Engineering Design, 3rd Edition; BP Amoco and Toray product literature.

As the solution exits the spinneret, it enters a coagulation bath where the copolymer precipitates into filament form. The filaments are made up of a finer structure, termed "fibrils," which run parallel to the filament axis. Various processing parameters, such as coagulation bath temperature, solvent concentration, and degree of stretch, can influence the fibrillar structure and its orientation within the as-spun PAN fiber. In other words, wet spinning yields a precursor fiber in which the PAN molecules are organized into fibrils that, in turn, are generally oriented parallel to the fiber axis. The bundle of filaments (referred to as a tow) is then washed to remove excess solvent and stretched to enhance molecular orientation. This step is essential for producing a final carbon fiber with adequate strength and modulus. Like most polymeric fiber processes, stretching does not greatly increase the crystallinity, which is a maximum of 50 percent, or the molecular order within the PAN fiber; rather, it enhances the axial orientation. This fibrillar network appears to be the precursor of the graphene network that develops during final heat treatment.

The PAN precursor fiber is converted to a carbon fiber in two separate process steps. In the first step, the fiber is heated in air to cross-link the structure. This renders the fiber infusible and inhibits relaxation of the structure during the final heat treatment step. In this step, termed carbonization, a standard-modulus fiber is heated in an inert environment to temperatures approaching 1400°C; higher-modulus fibers may be processed up to 2600°C. This step drives off most of the non-carbon elements, creating a carbon fiber. Since the PAN precursor is approximately 67 percent carbon, it is not surprising that the overall process conversion efficiency for PAN-based fibers (pounds of carbon fiber per pound of precursor fiber) ranges from 50 to 60 percent.

PAN-based precursor fibers continue to be produced using fundamental technology developed in the 1960s. Since then, fiber properties have improved significantly. Tensile strengths have more than doubled, from 2.8 GPa (400 kpsi) to more than 5.5 GPa (800 kpsi), and fiber with 290 GPa (42 Mpsi) has

[4] D.D. Edie and R.J. Diefendorf. 1993. Carbon fiber manufacturing. Carbon-Carbon Materials and Composites. J.D. Buckley and D.D. Edie, eds. Park Ridge, N.J.: Noyes Publications, pp. 19-37.

been introduced.[5] Until the 1980s, special acrylic fiber (SAF) precursor was used for nearly all PAN-based carbon fibers. This precursor fiber is produced in tow sizes of 3,000, 6,000, and 12,000 filaments and is normally supplied on spools without applying a crimp or twist. However, the emergence of non-defense, non-aerospace markets increased the demand for fibers with acceptable properties at a lower price. This led, in part, to the introduction in the early 1990s of large PAN staple tows as precursor material that contains up to 320,000 individual filaments. These large staple tows, originally developed for the textile industry, must be crimped in order to be handled effectively, but this allows the manufacturer to increase the throughput of fiber, resulting in a lower-cost product. However, the defects inserted by crimping, as well as the difficulty in maintaining uniform tension, small oxygen concentration gradients, and a uniform temperature profile, result in carbon fibers from the large textile tows having slightly lower mean strength and greater strength and stiffness variability compared to SAF-based materials.

### *Pitch-Based Carbon Fiber*

Like PAN-based carbon fibers, the peculiarities of pitch-based fibers are the direct result of the precursor and the process used to convert it to fiber form. In this case, the precursor is mesophase pitch, a liquid crystalline material consisting of large polynuclear aromatic hydrocarbons derived from petroleum or coal. The first commercial mesophase precursors were produced by Union Carbide using a thermal polymerization process.[6] The precursors were prepared by thermally polymerizing (using an inert gas sparge) a highly aromatic isotropic pitch feed at temperatures of 400 to 410°C for as long as 40 hours. The shear forces during extrusion and subsequent drawing produce a filament with high molecular orientation in the direction of the fiber axis. This orientation is maintained during oxidation and high-temperature carbonization. Carbon fiber can be produced in this way with a variety of strength and flexibility characteristics.

Mitsubishi Gas Chemical Company commercialized a process that uses a strong Lewis acid catalyst (hydrogen fluorene-boron fluorene, HF-$BF_3$) to catalyze a pure chemical feed, such as naphthalene or methylnaphthalene, to a 100 percent mesophase product. The use of HF-$BF_3$ has been shown to greatly reduce the molecular weight distribution of the mesophase product compared to that produced by thermal polymerization.[7]

ConocoPhillips also developed a process for producing a mesophase carbon fiber precursor.[8] The extraction step removed the smaller disordering molecules and concentrated the higher-molecular-weight material. The higher-molecular-weight fraction was then converted to 100 percent mesophase by multiple, brief, heat treatment steps. The final product consisted of a high-molecular-weight mesophase containing a small fraction of solvent that effectively served as a plasticizer.

The mesophase products resulting from these three processes differ considerably; for example, each process yields a product with a different molecular weight distribution (the averages range from 800 to 1,200 daltons) and a different concentration of aliphatic side chains on the individual mesophase molecules. Consequently, their viscosity characteristics differ and their rate of stabilization differs as well. Nevertheless, all of these mesophase products reach a viscosity of approximately 200 pascal-seconds, well below their degradation temperature, allowing them to be melt-spun into fiber form. Also, although somewhat irregular, all of the individual mesophase molecules are disk-like in shape.

In the melt-spinning process, the solid feed is melted and forced through a spinneret. As the molten precursor exits these holes, it is simultaneously quenched by the surrounding atmosphere and drawn down by the take-up device, forming solid fibers. At first glance, this would appear to be a relatively simple process; however, the results are extremely sensitive to small changes in process conditions. Under typical process conditions, the tensile stress on mesophase fibers is about 20 percent

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[5] Tensile strengths are generally reported in gigapascals (GPa) or thousand pounds per square inch (kpsi). For very large numbers, million pounds per square inch (Mpsi) is also used.

[6] L.S. Singer. 1977. High modulus high strength fibers produced from mesophase pitch. U.S. Patent 4,005,183. I.C. Lewis. 1977. Process for producing fibers from mesophase pitch. U.S. Patent 4,032,430. S. Chwastiak. 1980. Low molecular weight mesophase pitch. U.S. Patent 4,209,500.

[7] I. Mochida, K. Shimizu, Y. Korai, H. Otsuka, Y Sakai, and S. Fujiyama. 1990. Preparation of mesophase pitch from aromatic hydrocarbons by the aid of HF/$BF^3$. Carbon 28(2):311-319.

[8] W.M. Kalback, H.E. Romine, and X.M. Bourrat. 1991. Solvated mesophase pitches. U.S. Patent 5,259,947.

of that required to break the fiber.[9] (In comparison, during melt spinning the tensile stress developed within a nylon fiber is less than 1 percent of the breaking strength of the filament.) This greater tensile stress in the mesophase fibers is a direct result of two peculiarities of mesophase: its highly temperature-dependent viscosity and the brittle nature of as-spun mesophase fibers.

Because their viscosity is highly temperature dependent, mesophase pitch fibers draw down and cool very quickly during fiber formation. In fact, at typical melt-spinning conditions, mesophase fibers are already 100°C below their glass transition temperature by the time they are 2 cm from the spinneret. As a result, they can break easily during spinning and are extremely difficult to handle before they are carbonized. Although the rheology of mesophase makes control of the melt-spinning process more difficult, its liquid crystalline nature gives this precursor structural advantages compared to polymeric precursors such as PAN.

The pitch precursor fiber is converted to a carbon fiber in two separate process steps. Like PAN precursor fibers, the fiber is initially heated in air to cross-link the structure. This renders the fiber infusible and inhibits relaxation of the structure during the final heat treatment step. However, the pitch fiber (unlike the PAN fiber) is extremely weak at this stage, which makes it difficult, if not impossible, to pull it through the oxidation oven (the technique used in PAN-based carbon fiber process). This problem has led to alternate oven designs and advanced fiber-handling techniques.

In the final heat treatment step—termed carbonization—the fiber is heated in an inert atmosphere to temperatures as high as 3000°C. This drives off most of the non-carbon elements, creating a highly oriented carbon fiber with truly graphitic crystallinity. Since the mesophase precursor is approximately 90 percent carbon, the overall process conversion efficiency for pitch-based fibers (pounds of carbon fiber per pound of precursor fiber) can be much greater than PAN-based carbon fibers. However, the brittle nature of pitch fibers leads to increased breakage during processing, often lowering the actual process conversion.

Since the first development of mesophase precursors, researchers have recognized that melt-spun mesophase fibers can develop remarkably high elastic moduli. This is a direct result of the transverse microstructure and axial molecular orientation created as the liquid crystalline precursor flows through a capillary and then is extended during fiber formation. Unless relaxation occurs during thermosetting, the transverse microstructure and axial orientation are merely perfected during carbonization. The transverse microstructural texture of early commercial mesophase carbon fibers was either radial or flat layer. Thus, in the transverse direction the graphene layer planes fan out from the center of the fiber, and in the axial direction the layer planes tend to align parallel to the fiber axis.

Mesophase pitch-based carbon fibers with radial and flat-layer transverse textures readily develop three-dimensional crystallinity. Although this structure makes these pitch-based carbon fibers more flaw sensitive than PAN-based fibers with their more random, filament structure, it gives them superior lattice-dependent properties (modulus and thermal conductivity).

Figure 1.3 shows that prior to 1990, PAN-based carbon fibers were characteristically high strength but low modulus, whereas pitch-based carbon fibers were high modulus but low strength. Since then, manufacturers have discovered that they can disrupt flow during extrusion and create mesophase precursor fibers with random transverse textures. This disrupted texture mimics the filament texture of PAN-based fibers by reducing flaw sensitivity. This, in addition to developing purer mesophase precursors, has allowed the introduction of new varieties of pitch-based carbon fibers with improved tensile strengths.

Similarly, manufacturers such as Cytec have begun using improved mesophase precursors and linearizing the transverse texture during extrusion to create new varieties of pitch-based carbon fibers with thermal conductivities that are at least three times that of copper.[10] Most agree that these highly ordered textures can be produced only by using a liquid crystalline precursor. Thus, this new product may represent the natural niche for mesophase pitch-based carbon fibers.

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[9] D.D. Edie and M.J. Dunham. 1989. Melt spinning pitch-based carbon fibers. Carbon 27(5):647-655.

[10] J.G. Lavin, D.R. Boyington, J. Lahijani, B. Nysten, and J.P. Issi. 1993. The correlation of thermal conductivity with electrical resistivity in mesophase pitch-based carbon fiber. Carbon 31(6):1001-1002.
N.C. Gallego and D.D. Edie. 2000. The thermal conductivity of ribbon-shaped carbon fibers. Carbon 38(7):1003-1010.

### *Rayon-Based Carbon Fibers*

Rayon was the original precursor for carbon fibers. Like PAN, rayon precursor fibers are solution spun, then stabilized and carbonized to form carbon fibers. High tension is often applied during the final step (termed stress graphitization) to increase the modulus and strength of rayon-based carbon fiber. The solution spinning process gives rayon-based carbon fibers a crenulated cross section, a peculiarity that appears to improve the performance of carbon-carbon composites. Stress graphitization and the low carbon content of the precursor account for the high cost of this type of carbon fiber.

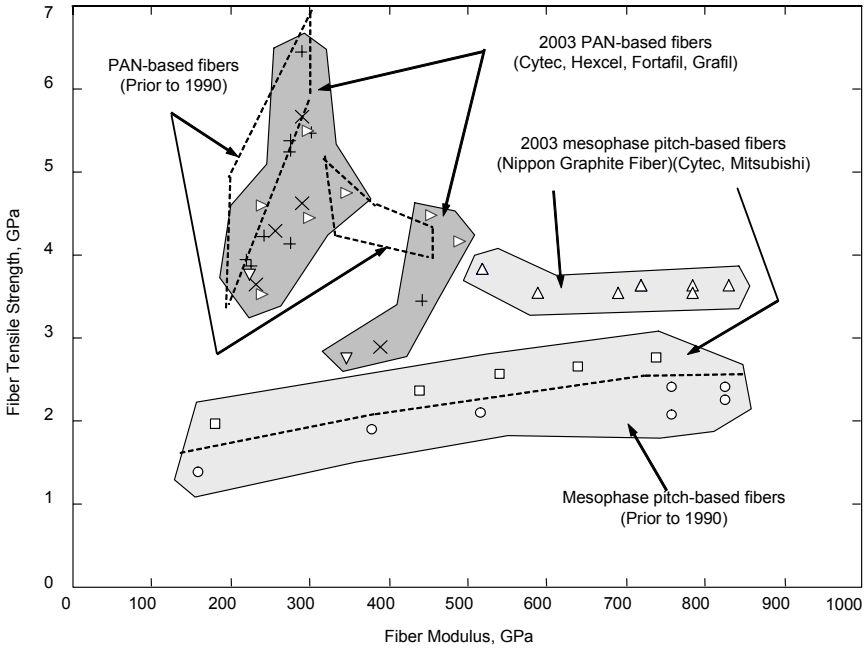


FIGURE 1.3 Improvement of the mechanical properties of commercial PAN-based and mesophase pitch-based carbon fibers from the period prior to 1990 to 2003. DATA SOURCES: Historic and current corporate product literature.

Rayon-based carbon fibers are used predominantly for ablative applications such as reentry vehicle nosetips, heat shields, and solid-rocket motor nozzles and exit cones. These applications require high thermal resistance but relatively low strength. The tensile strengths of these fibers vary from 345 to 690 MPa (50 to 100 kpsi) and the tensile moduli range from 20 to 55 GPa (3 to 8 Mpsi). Because of their relatively low tensile strength and high cost, rayon-based carbon fibers have been largely supplanted by PAN-based carbon fibers.[11]

### *Microstructure-Dependent Properties of Carbon Fibers*

Figure 1.3 shows the trade-off between tensile strength and modulus for each class of fibers and illustrates the improvements in properties of commercial PAN-based and pitch-based carbon fibers achieved during the 1990s. The reason for the significant differences in modulus and strength lies in the structure of the fibers. X-ray studies prove that PAN-based carbon fibers have no long-range, three-dimensional order.[12] Instead, PAN-based carbon fibers contain extensively folded and interlinked turbostratic layers of carbon with interlayer spacings considerably larger than that of graphite. As a result, PAN-based carbon fibers have a low degree of graphitization. The turbostratic layers in PAN-based carbon fibers appear to follow the original fibrillar structure of the PAN precursor fiber. Although the turbostratic layers within these filaments tend to be oriented parallel to the fiber axis, they are not highly aligned. In contrast, pitch-based fibers are composed of highly oriented graphene sheets parallel to the fiber axis. Transverse to the fiber axis the sheets can be arranged radially, randomly, or in a flat-layer structure. Pitch-based fibers have a larger crystallite size as well.

Thus, pitch-based fibers have a higher modulus because of the high degree of orientation in the fibers compared to PAN-based fibers. Pitch-based fibers have lower strength because the high degree of graphitization also leads to larger crystallites. Carbon fibers fail due to the failure of internal defects in the form of these crystallites. The smaller a crystallite is, the less likely its failure is to cause catastrophic failure in the fiber.

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[11] Chemical Economics Handbook. 1999. Menlo Park, Calif.: SRI Consulting.

[12] D.J. Johnson. 1987. Structure property relationships in carbon fibers. Journal of Physics D: Applied Physics 20(3):287-291.

Recent work indicates that the intercrystalline and intracrystalline disorder characteristics of PAN fibers are also responsible for the superior compressive strength of this type of carbon fiber. Thus, the same fibrillar morphology that disrupts the transverse structure of PAN-based carbon fibers and gives them a higher tensile strength than pitch-based fibers also gives PAN-based fibers superior compressive properties. In other words, polymeric precursor fibers, such as PAN fibers, offer natural advantages when compression properties are critical. Developing superior compressive properties in pitch-based carbon fibers could be much more difficult.

As Figure 1.3 shows, the tensile strengths of pitch-based carbon fibers improved significantly during the 1990s, whereas the strengths of PAN-based fibers, although higher than those of pitch-based fibers, remained relatively constant for two reasons. The obvious reason is that the lower strength of early pitch-based fibers offered more opportunity for improvement. However, the major reason is that pitch-based carbon fiber producers have developed better mesophase pitch precursors and learned how to control the molecular structure of the precursor during fiber formation. The results have been improved properties and potentially lower production costs.

Nevertheless, the natural application of mesophase pitch-based fibers is not in high-strength applications, but in those requiring high thermal conductivity. This is because linearizing the pitch fiber's transverse structure to produce high thermal conductivity (approximately 100 times greater than PAN-based fibers) is easier than disrupting the structure enough to significantly increase the tensile strength. Furthermore, pitch-based carbon fibers are generally capable of achieving higher moduli compared to PAN-based fibers, making them attractive for stiffness-critical applications such as certain spacecraft components. Thus, for the foreseeable future, it is likely that PAN-based fibers will dominate applications where strength is critical, and pitch-based fibers will dominate applications where heat transfer or stiffness is important.

## HIGH-PERFORMANCE ORGANIC FIBERS

The precise definition of high-performance organic fibers is controversial. High-performance functionalities may include high strength, high stiffness, high toughness, damage tolerance, durability, dimensional stability, and flame resistance. Often, more than one of these properties is required in a single fiber. High strength and stiffness require almost perfectly oriented polymer molecules and a fully extended polymer chain. Although this has been recognized since the 1930s, the breakthrough in producing a highly oriented aramid fiber did not occur until the late 1960s and early 1970s when it was discovered that nematic solutions of poly(*p*-benzamide) and poly(*p*-phenylene terephthalamide) could be processed into fibers with a highly oriented, extended chain configuration.[13]

Commercial high-performance organic fibers first became available with the introduction of a *meta*-aramid (*m*-aramid) fiber, Nomex, in the second half of the 1960s. Since that time, several classes of fibers have been commercialized. High-strength *p*-aramid fibers were introduced in the early 1970s, followed by liquid crystalline polyesters (LCPs), high-strength polyethylene, and most recently, the introduction of poly(*p*-phenylene-2,6-benzobisoxazole), or PBO. A new fiber M5® has entered late development stages. Table 1.1 summarizes properties of existing commercial organic fibers, while Figure 1.4 compares the properties of these fibers with those of other materials. Both strength and stiffness are expressed as specific values and are corrected for density.

### *meta-Aramids*

*meta*-Aramid fibers (especially with 100 percent aromatic content) offer very high temperature stability. Homopolymers in this class of materials exhibit a glass transition temperature of 275°C and a melting temperature of 420°C, very close to the decomposition temperature. The high aromatic content is also responsible for excellent performance in flame, leading to an intumescent char with adequate mechanical properties to provide for additional thermal insulation. The thermal stability and fire resistance characteristics of *m*-aramid fibers make them attractive for application such as protective apparel and hot gas filtration.

[13] V. Gabara. 1994. High performance fibers 1: aramid fibers. Synthetic Fibre Materials, H. Brody, ed. New York: Longman Publishing Group, pp. 239-260.

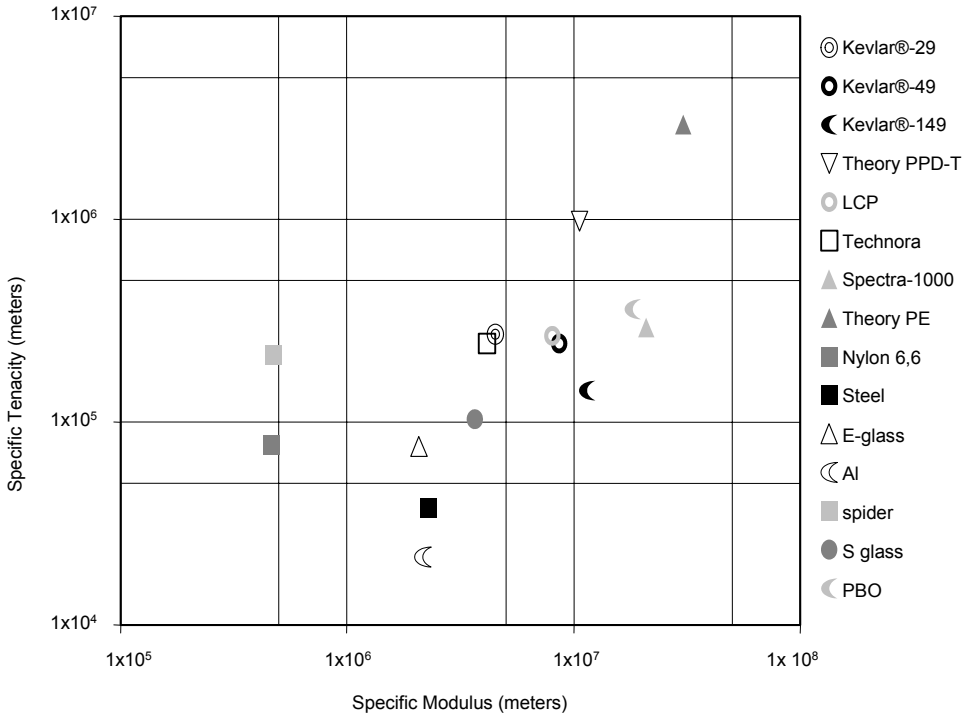


FIGURE 1.4 Specific tenacity versus specific modulus for several advanced organic fibers. DATA SOURCE: Composites Design. Available at http://www.carb.com/carbon_comp.html. Accessed September 2004.

These fibers are now also being marketed in paper form, making them attractive for structural applications. *m*-Aramid-based paper can be saturated with a matrix (e.g., epoxy, phenolic) resin to form composite boards, or it can be converted into honeycomb structures, which find applications in the aerospace, electrical, and electronic industries. For example, Nomex products are used in protective apparel, hot gas filtration, automotive hoses, electrical insulation, aircraft parts, and sporting goods.

### *para-Aramids*

This class of materials has several products differing in the specific chemistries used. The first commercial product (Kevlar) is based on *p*-(phenylene terephthalamide), which continues to represent the largest global volume. The same chemistry underlies the second-largest-volume product, Twaron. Due to the rigidity of this material it forms anisotropic solutions in its solvent, sulfuric acid. The air-gap spinning process converts the solution into a highly ordered, highly crystalline fiber. This higher rigidity translates into better thermal properties (dimensional stability). Several *p*-aramid copolymers have been evaluated in the past. As copolymers, they are noncrystalline and can be processed by spinning from organic solvents containing salts with orientation, and thus properties, developed by fiber drawing. Technora represents the only firm that has reached a small commercial scale in the West. Russian scientists had structured their *p*-aramids (SVM, Armos, Rusar) on a rather expensive monomer diaminophenylbenzimidazole and its copolymers with *p*-phenylenediamine. This technology while producing slightly better mechanical properties, results in a very expensive fiber (monomer cost, very low productivity spinning processes, and very large energy consumption). Many of these products still do not meet Western standards as far as quality and uniformity are concerned.

*p*-Aramids, such as Kevlar fibers, are used in thermal-resistant clothing, protective vests and helmets, composites, asbestos replacement, reinforcement for tire and mechanical rubber goods, ropes and cables, and sporting goods.

TABLE 1.1 Mechanical Properties of Some Fibers, Including Projections for M5®

| Fiber | Strength (σ) (GPa) | Failure Strain (ε) (%) | Modulus (*E*) (GPa) | $(U^*)^{1/3}$ [a] (m/s) |
|---|---|---|---|---|
| PBO[b] | 5.20 | 3.10 | 169 | 813 |
| Spectra 1000 | 2.57 | 3.50 | 120 | 801 |
| 600-den.[c] Kevlar KM2 | 3.40 | 3.55 | 82.6 | 682 |
| 850-den. Kevlar KM2 | 3.34 | 3.80 | 73.7 | 681 |
| 840-den. Kevlar 129 | 3.24 | 3.25 | 99.1 | 672 |
| 1,500-den. Kevlar 29 | 2.90 | 3.38 | 74.4 | 625 |
| 200-den. Kevlar 29 | 2.97 | 2.95 | 91.1 | 624 |
| 1,000-den. Kevlar 29 | 2.87 | 3.25 | 78.8 | 621 |
| 1,140-den. Kevlar 49 | 3.04 | 1.20 | 120 | 612 |
| Carbon fiber | 3.80 | 1.76 | 227 | 593 |
| E-glass | 3.50 | 4.7 | 74.0 | 559 |
| Nylon | 0.91 | N/A | 9.57 | 482 |
| M5 conservative | 8.50 | 2.5 | 300 | 940 |
| M5 goal | 9.50 | 2.5 | 450 | 1,043 |
| M5 (2001 sample) | 3.96 | 1.4 | 271 | 583 |

[a] U* is the product of fiber specific toughness and strain wave velocity such that the dimensional analysis indicates that V50 velocity of an armor system scales with $(U^*)^{1/3}$.
[b] poly(*p*-phenylene-2,6-benzobisoxazole)
[c] denier
SOURCE: P.M. Cunniff, M.A. Auerbach, E. Vetter, and D.J Sikkema. 2004. High performance "M5" fiber for ballistics/structural composites. Paper AO-04 at the 23rd Army Science Conference. Available at http://www.asc2004.com/23rdASC/manuscripts/A/AO-04.PDF. Accessed September 2004.

### *Liquid Crystalline Polyesters*

Development of LCPs followed commercialization of *p*-aramids. Like the *p*-aramids, LCPs are based on aromatic structures. Finding a balance between processibility and properties has been a constant challenge for this technology. To achieve melt processibility into fibers, various copolymer compositions have been used and materials have to be spun at low molecular weight. To obtain adequate physical properties, a slow heat treatment process has to be applied. While the strength and stiffness of fibers in this class are of the same order of magnitude as aramids, their thermal properties are somewhat lower. LCP fibers are used in applications such as tow ropes, cargo tie-downs, tethers, and cables.

### *High-Strength Polyethylene*

Ultrahigh-molecular-weight polyethylene (UHMWPE) offers the first demonstration that the fully extended chain configuration and resultant high-performance properties can be achieved in flexible polymers. The shaping process is relatively complex. Gel spinning at low polymer concentration is followed by extraction of the solvent and the critical drawing step. The very high draw ratio achievable in this system is responsible for the development of high strength and stiffness of the fiber.[14] However, the low melting point of this material limits its applicability at elevated temperatures, and its nonpolar nature decreases its adhesion to resins.

[14] D.C. Prevorsek. 1994. High performance fibers 2: High performance polyethylene fibers. Synthetic Fibre Materials, H. Brody, ed. New York: Longman Publishing Group, pp. 263-285.

TABLE 1.2 Physical Properties of Some Organic Commercial Fibers

| | *p*-Aramid | UHMWPE[a] | PBO[b] |
|---|---|---|---|
| Yarn tenacity, gpd[c] | 18-27 | 30-38 | 40-42 |
| Density, g/cm$^3$ | 1.44 | 0.97 | 1.56 |
| Moisture regain, percent | 1-7 | 0 | 0.6-2 |
| Heat resistance, °C | 550 | 150 | 650 |
| LOI[d], percent | 29 | 20 | 68 |

[a] ultrahigh-molecular-weight polyethylene
[b] poly(*p*-phenylene-2,6-benzobisoxazole)
[c] grams per denier
[d] limiting oxygen index
SOURCE: Chemical Economics Handbook. 1999. Menlo Park, Calif.: SRI Consulting.

Spectra fibers are used in numerous applications, including ballistic vests, helmets, armored vehicles, sailcloth, fishing lines, marine cordage and lifting slings, and cut-resistant gloves and safety apparel. Ballistic applications have become important for this material since the development of unidirectional composite laminated structures, which allow for diminishing blunt trauma.

### *PBO*

The invention and development of high-performance fibers based on aramids led to an understanding of principles underlying this area of science and technology. The natural extension was to move to even more rigid polymers. The development of PBO and PBZT (polyphenylene benzobisthiazole) compositions by Wolf and others, with the continuing work of Dow Chemical Company and finally Toyobo, culminated in commercialization of Zylon fiber in the second half of the 1990s. Toyobo expects to increase the capacity of this fiber to 500 megatonnes by 2007.

As for other rigid polymers, the shaping of this fiber is through processing of anisotropic solutions, but this time from polyphosphoric acid. Higher rigidity than aramids and lack of amide bond translate to improved thermal properties and improved mechanical properties (Table 1.2). Expensive ingredients and highly aggressive solvent combined with the extremely high viscosities of these solutions result in significantly higher prices versus aramid fibers.

While the advantages previously cited are generically associated with very rigid polymers, some disadvantages are due to specific chemistries. Poorer ultraviolet (UV) stability and adhesion to resins limit its use in some applications. More recently, there have been reports of some possible problems with hydrolytic stability. This issue is important enough to warrant careful following of future developments.

### *M5® Fiber*

Although the fibers previously discussed are produced at very different volumes, the entire set is considered commercial. The committee has given significant consideration to one fiber, which is in the precommercial stage of development, M5 (poly{2,6-diimidazo[4,5-*b*:4',5'-*e*]pyridinylene-1,4-(2,5-dihydroxy)phenylene}), or PIPD.[15] The fiber is being developed by Magellan Systems International, which expects to start up a pilot plant in 2005, with a commercial facility likely in 2007. M5 is a rigid polymer spun from an anisotropic solution; its properties are given in Table 1.3. While the tensile properties realized are similar to those of PBO, the fiber offers potential for significant improvement of compressive properties above those of any of the commercial organic fibers. The compressive strength of the fiber ranges from two to four times that of other organic fibers. This is attributed to the higher level of hydrogen bonding, which improves its structural integrity. Such properties offer potential for combining both structural and ballistic requirements of systems. This is further strengthened by a very good adhesion to resins (imidazole group) and, thus, improved performance in composite applications. The differences

[15] Advanced Lightweight Engineering. 1998. M5 materials research. Available at http://www.lightweight.nl/akzo.htm. Accessed March 2005.

TABLE 1.3 Properties of M5® Fiber

| Fiber | PBO Zylon[a] | M5 1999-2000 | M5 April 2002 | M5 Targets |
|---|---|---|---|---|
| Tenacity, GPa | 5.5 | 4 | 5.3 | 9.5 |
| Elongation, % | 2.5 | 1.2 | 1.5 | >2 |
| Elastic modulus, GPa | 280 | 330 | 350 | >400 |
| Compressive stress[b], GPa | 0.42 | 1.6 | 1.7 | 2 |
| Compressive strain[b], % | 0.15 | 0.4 | 0.5 | 0.5 |
| $\sigma_{max}$ compressive, GPa[c] | 0.8 | 3 | 3 | 4 |
| Density, g/mL | 1.56 | 1.7 | 1.7 | 1.7 |
| Water regain, % | 0.6 | 2.0 | 2.0 | 2 |
| Onset of thermal degradation in air, °C | 550 | 530 | 530 | 530 |
| LOI[d], $\%O_2$ | 68 | >50 | | >50 |
| Electrical conduction | – – | – – | | – – |
| Impact resistance, composites | ++ | ++ | | +++ |
| Damage tolerance | N/A | ++ | | +++ |
| Weaving properties | +/– | + | | + |
| Stability in UV radiation | – – | ++ | | ++ |

[a] Toyobo data, available at http://www.toyobo.co.jp/
[b] Measured in unidirectional composite test bars, three-point bending test, onset of deflection for the organic fiber reinforced composites; catastrophic failure for the carbon composites. M5 composites proved to be able to carry much higher loads than the load at onset of deflection and to absorb much energy at high strains in a mode analogous to the flow behavior in steel being damaged.
[c] In a bending test on unidirectional composites, the maximum apparent stress on the outermost fibers (neglecting change of shape, at the compression side, by ductile response at high deformation).
[d] limiting oxygen index
SOURCE: Magellan Systems International.

between oxazole and imidazole rings results in better UV stability and potential for improved hydrolytic stability.

The high-performance fibers that are currently available have been in production for decades, and the technology is now mature. Their properties depend sensitively on microstructure and in some cases are approaching theoretical limits. Thus, for commercial fibers only incremental improvements in fiber properties are expected in the near future. The new fiber M5, which is in precommercial development, offers a potential for a unique combination of properties that promises a unique set of applications.

### *Raw Materials for Organic Fiber Development*

The development of advanced organic fibers is a complex and expensive endeavor. It usually requires the establishment of a raw materials base in addition to processes for polymerization and shaping. Of the fibers discussed in this report, only UHMWPE did not require the introduction of a new raw material. Raw materials and their development represent a significant portion of the cost associated with the development of advanced fibers. For example, PBO fibers are extremely expensive because of the expensive ingredients required to produce them, despite the fact that the development of these fibers began approximately 20 years ago. The need to develop an ingredients base is also essential to successful commercialization of M5 fiber.

### *Properties and Design Needs*

It is well established that the thermal properties of organic fibers are controlled by the chemistry and morphology of the fibers and that little can be done to improve these properties within a given chemical composition. Therefore, it is important to choose a material that can maintain its properties over the expected operating temperature range. On the other hand, the mechanical properties of all materials in Table 1.1 can be tailored to meet the needs of specific applications. A good example of such tailoring

can be found in the aramid family, where production technology has been developed to alter the balance between the elongation and modulus of fibers to meet the demands of applications that are driven by fatigue (e.g., reinforcement of rubber) as well as polymer matrix composite applications, where stiffness is a controlling factor. These two extremes cover the range of elongation and modulus described in Table 1.2.

Current estimates of theoretical strength and stiffness for *p*-aramids and polyethylene are shown in Figure 1.4. The elastic modulus realized in commercially available fibers approaches 80 percent of the theoretical values for these fibers. Thus, a dramatic increase in the stiffness of these organic fibers is not expected. For higher stiffness, one would have to look at the fibers described in Table 1.3. Estimating the theoretical strength of a material is more difficult and less reliable than estimating the theoretical modulus. However, there is general agreement that the strength values attained for organic fibers are further from theoretical values than are the modulus values. For example, demonstrated values of strength are estimated at 30 to 50 percent of theoretical expectations. Thus, it is reasonable to expect incremental improvements in strengths of existing commercial fibers over the next several years.

# 2

# Fibers in Composites

Although fibers have many of the desired properties that are needed for military, aerospace, and commercial applications, they generally act as part of a composite system. The matrix protects the fibers from the environment, and both the matrix and the interface transmit external stresses to the fibers. Therefore, the overall properties of composite structures depend on the properties of the individual components (fibers, matrix, and the interfacial region connecting them) as well as the processes and methods used to fabricate the finished structures. We are only beginning to understand how fiber properties can be translated into superior properties of the overall composite.

## MATRIX RESINS

Although the fibers play a dominant role in determining the stiffness and strength of a composite, the choice of the matrix will determine maximum service temperature, viable processing approaches, and long-term durability. Matrix materials can be divided into two broad categories: thermosetting and thermoplastic. Thermosetting materials are characterized by having a low-viscosity, reactive, starting oligomer that cures (reacts) to form an insoluble, infusible network.[1] The cure temperature and time influence many matrix properties. An incomplete cure affects mechanical properties, swelling behavior in solvents, and moisture susceptibility. On the other hand, an incomplete cure (increased distance between cross-links) may improve flexibility and toughness.

Thermoplastics are linear or slightly branched polymers of relatively high molecular weight. They are of significant interest because they can be remelted, thus easing repair in the field, and because they are melt-processable. The use of thermoplastics also allows other composite processing techniques such as injection molding of short fiber composites and extrusion of long fiber composites. Thermoplastic polymer morphology may be either amorphous (disordered) or semicrystalline (partially ordered). The semicrystalline and even liquid crystalline morphologies can impart superior solvent resistance to the overall matrix resin. Semicrystalline polymers display a melting temperature for the crystalline regions as well as a glass transition, and processing must be performed in excess of the melting temperature. Amorphous thermoplastics, on the other hand, are processed above the glass transition temperature. A possible limitation for some applications of semicrystalline polymers concerns the morphological changes that may occur during processing or in the service environment, particularly due to the application of heat or exposure to solvent while under stress. These changes in the crystalline structure and/or content may cause changes in the overall composite properties and are highly undesirable. Likewise, control of morphology during processing is critical to achieving the desired matrix properties such as toughness and chemical resistance.

Various resins exist today that provide a wide range of service temperatures. For example, epoxies, vinyl esters, and polyesters will meet the relatively low-service-temperature requirements (160 to

[1] A. Knop and L.A. Pilato. 1985. Phenolic Resins: Chemistry, Applications, and Performance. Berlin: Springer Verlag.

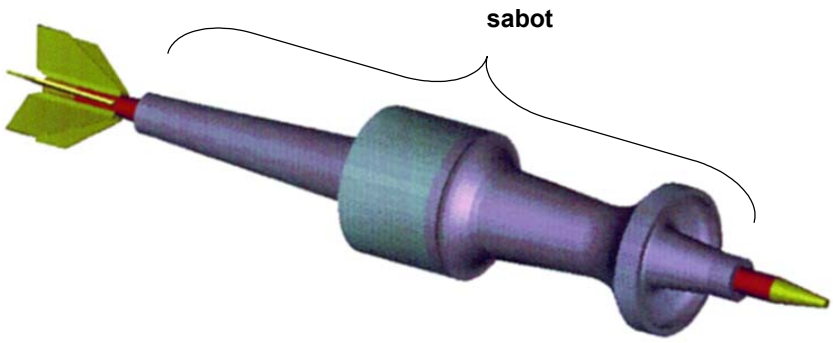


FIGURE 2.1 The M829A2 sabot, which stabilizes the trajectory of the munition early in flight, was designed with graphite fiber-reinforced epoxy material that resulted in a 30 percent weight reduction in the sabot component. This weight reduction enabled an increased muzzle velocity of approximately 60 meters per second, significantly increasing the range and armor penetration capability of the projectile. The M829A2 accounts for one of the largest uses of composite materials in DoD. DATA SOURCE: Army Research Laboratory. Description available at http://www.arl.army.mil/wmrd/Tech/AntiArmor-both.pdf. Accessed March 2005.

180°F) of the Army's Future Combat System ground and tactical vehicles as well as Navy ship systems. Vacuum-assisted resin transfer molding (VARTM) has been identified as an affordable process and is used to fabricate structural armor for ground vehicle hull structures containing integral ceramic composites, as well as large-scale topside ship and hull structures. Desirable resin attributes for these applications include relatively low viscosity at room temperature to enable room-temperature infusion as well as the lowest cure temperature possible to meet hot-wet glass transition temperature requirements. Resins meeting these needs enable low-temperature tooling materials to be used, providing significant cost savings. However, the performance demands on these composites remain high. For example, structural armor requires resins that have high elongation to failure to survive ballistic impact, but current VARTM resins fall short of the service temperature requirement. Higher-cure-temperature resins meet service temperature requirements, but ballistic performance is degraded. Additional research in resins is needed to balance processing ease and performance for these important Department of Defense (DoD) applications.

Higher-temperature performance can be achieved (250 to 400°F) with epoxies, bismaleimides, and polyimide resins using traditional prepreg or towpreg[2] and autoclave, filament winding, and fiber placement process technologies. Formulations of these materials have been developed to enable the use of resin transfer molding (RTM) processes for smaller-scale components.

The need for more damage-tolerant aerospace structures has led to the development of toughened thermosets and thermoplastic matrices that are resistant to impact damage and delamination growth. High matrix toughness has also been proven to be a key property in ballistic performance of tank munitions such as the M829A2 (toughened thermoset) and the M829A3 (polyetherimide thermoplastic) carbon fiber sabots (see Figure 2.1). The capability of electron-beam (e-beam) processing for non-autoclave cure of large-scale structures such as rocket motors and fuel tanks has been demonstrated. Improvements in resin toughness and interface optimization for e-beam resins are needed to improve properties and resistance to microcracking.

The role of the matrix in the long-term durability of a composite is a critical issue. Durability is affected by the state of the resin, which may undergo physical aging or environmental degradation, as well as changes in the interaction with the fiber at the interface. In addition, the stress state within the matrix due to processing, thermal and fatigue cycling, and other mechanical loads is critical to the long-term performance. Microcracking is one of the first damage modes observed in the matrix phase. Microcracking can initiate fiber fracture, interface debonding, and delamination that can limit the lifetime of the component. An even more severe case occurs when microcracks provide pathways for accelerated

[2] Prepregs, or preimpregnated fiber assemblies, are commonly used in many applications and are fabricated by spreading an array of fiber tows and impregnating the tows with a thermoset or thermoplastic resin to produce a thin sheet of material. In this material form, the fibers are continuous and aligned, providing high stiffness and strength in the fiber direction and low matrix-dominated properties in the transverse direction. For structures subjected to multiaxial loadings, the prepreg is laminated to tailor the properties.

degradation by the environment, for example, moisture ingress into honeycomb structures followed by freeze-thaw or elevated temperature thermal oxidation that can dramatically reduce mechanical properties. Advances in modeling the failure mechanisms and the development of new microcracking-resistant composites are needed.

## FIBER-MATRIX INTERFACE

The interface can be defined as the three-dimensional boundary between the fiber and matrix. It is critical to controlling composite properties because fiber-matrix interaction occurs through the interface. This interaction can occur through three mechanisms: mechanical coupling or micromechanical interlocking of the two materials, physical coupling such as van der Waals or electrostatic interaction, and covalent bonding (by way of a coupling agent) between the fiber and the matrix (see Figure 2.2 for some examples). These interactions create an interphase region—which is a three-dimensional region near the fiber with properties different from either the fiber or the matrix. For example, in thermosets, the interphase can form due to preferential absorption of either the curing agent or the resin at the fiber surface, leading to a region of higher or lower cross-linking and in thermoplastics, the interphase can be a region of transcrystallinity. For ease of discussion, the term "interface" is used to describe both the two-dimensional interface and the three-dimensional interphase.

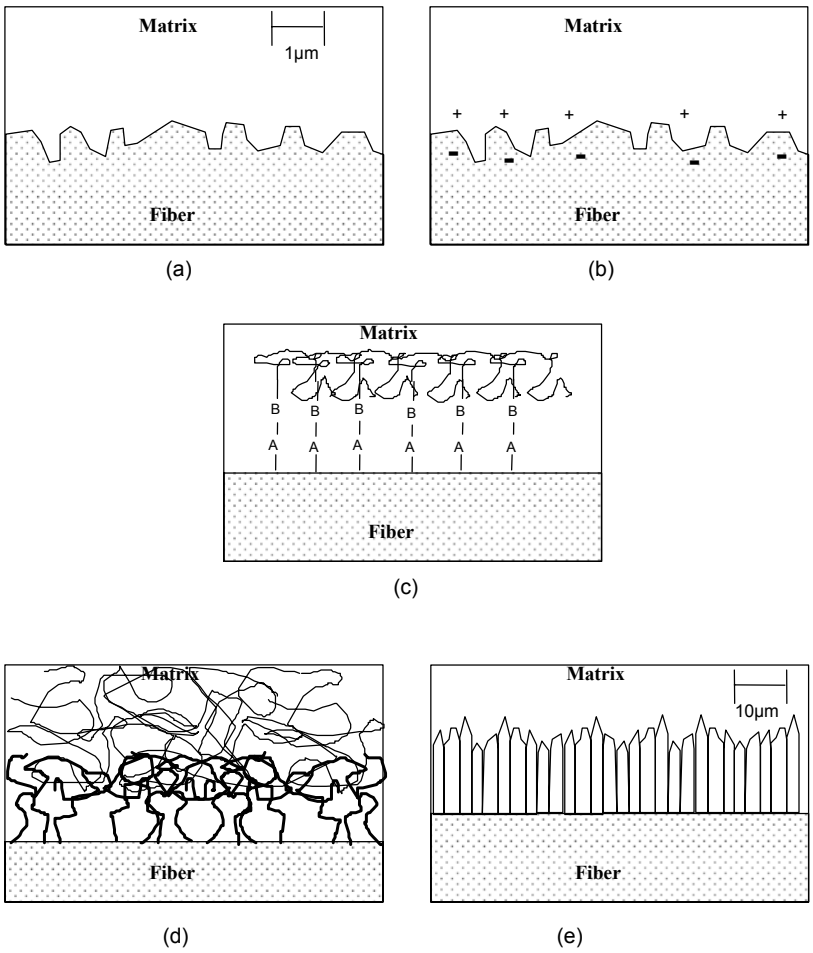


FIGURE 2.2 Schematic depictions of various interactions at the fiber-matrix interface: (a) micromechanical interlocking, (b) permanent or induced dipole interactions, (c) chemical bonding, (d) chain entanglement, and (e) transcrystallinity.

To control the properties of the interface, surface treatments are often used on the fiber. Surface treatment generally involves surface oxidation of the fiber, either electrolytically or using gas or liquid chemicals. This provides some functionality on the fiber surface by increasing the surface area and the number of reactive groups on the surface and can improve adhesion in terms of mechanical interlocking and physiochemical interactions. The surface can then be coated with different organic and/or inorganic compounds to promote further interaction. A sizing may also be used to protect the fiber from process damage. Some sizings, such as organosilanes, may also be referred to as coupling agents, as these couple the active fiber surface to a nonpolar resin, predominantly through increased oxygen functionality. Other types of materials, including oligomer polyimides and polyamides, can be grafted to the surface in order to promote adhesion through other mechanisms, such as transcrystallization.

The chemistry of such treatments is proprietary, but they may perform a variety of functions, as follows:[3]

- Protect the fiber surface during shipment and handling and subsequent processing,
- Bind the fibers together (which makes processing of prepreg and weaves easier),
- Reduce static electricity, and
- Improve the chemical bonding to the matrix.

While it is often assumed that the sizing improves the coupling between the fiber and the matrix, several studies have shown that sizing can create a brittle interface region.[4,5] Thus, sizings can be detrimental to bulk mechanical properties. In addition, sizings and other fiber treatments can lead to variability in the interface properties. This variability in interface properties can originate from several sources, including how evenly the sizing or coating covers the fiber; variability in wetting of the matrix that can create poorly bonded regions; variation in surface roughness of the fiber; and matrix variability.

The interface is crucial in controlling composite properties because load is transferred from the matrix to the fiber through the interface and deformation of the interface region (debonding or yielding) is critical in absorbing energy during failure.[6,7] In high-performance fiber-reinforced polymer matrix composites, the fiber has a much higher modulus than the matrix. Therefore, when the composite is loaded to a given strain, the fiber will carry more load than the matrix. This load must be transferred from the matrix to the fiber through the interface region.

The interface is particularly relevant in applications requiring damage tolerance and durability in aggressive environments,[8] because the interface controls damage development. When a fiber breaks, the neighboring fibers are subjected to a stress concentration.[9-11] The location of the next break due to the stress overload is dictated by the interface properties. Figure 2.2 shows some different types of interface bonding. Changing interface properties can have a dramatic effect on overload behavior. For the perfectly elastic case (from a strong interface), the stress concentration factor is large and narrow. This will lead to in-plane fiber failure and prevent energy absorbing mechanisms such as debonding and fiber pullout. Thus, brittle failure will occur. If the interface is compliant or debonding occurs, the stress concentration factor will decrease significantly and the region of overload in the neighboring fibers will be larger. This type of interface will lead to a brush-like fracture surface and higher ductility and toughness because of the debonding and fiber pullout that occur. In organic fibers, the fiber breaks are more diffuse and even the initial stress concentration is lower and more diffuse.[12] However, similar failure mechanisms apply. Thus a relatively weak interface contributes to high toughness for both organic and carbon fiber

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3 J.K. Kim and Y.W. Mai. 1998. Engineered Interfaces in Fiber Reinforced Composites. Oxford: Elsevier Science.

4 C. Marston and C. Galiotis. 1998. On the failure of unidirectional carbon-epoxy composites, Part I: The effect of fibre sizing upon filament fracture and damage evolution. J. Materials Science 33:5311-5325.

5 M.S. Amer, M. Koczak, and L.S. Schadler. 1996. Relating hydrothermal degradation in single fiber composites to degradation behavior in bulk composites. Composites 27A:861-867.

6 M.S. Madhukar and L.T. Drzal. 1992. Fiber-matrix adhesion and its effect on composite mechanical properties. III. Longitudinal (0 degree) compressive properties of graphite/epoxy composites, J. Composite Materials 26:310-333.

7 M.S. Madhukar and L.T. Drzal. 1993. Fiber-matrix adhesion and its relationship to composite mechanical properties. J. Materials Science 28:569-610.

8 B. Harris, P.W.R. Beaumont, and E. Mancunill de Ferran. 1971. Strength and fracture toughness of carbon fiber polyester composites. J. Materials Science 6:238-251.

9 P.W.J. van den Heuvel, T. Peijs, and R.J. Young. 1998. Failure phenomena in two-dimensional multi-fibre microcomposites—3. A Raman spectroscopy study of the influence of interfacial debonding on stress concentrations. Composites Science Technology 58:933-944.

10 L.S. Schadler and C. Galiotis. 1995. A review of the fundamentals and applications of laser Raman spectroscopy microprobe strain measurements in composite materials. J. International Materials Reviews 40:116-134.

11 C.D. Wagner, M.S. Amer, and L.S. Schadler. 1996. Fiber interactions in two-dimensional composites by micro Raman spectroscopy. J. Materials Science 31:1165-1173.

12 K.M. Atallah and C. Galiotis. 1993. Fiber strain mapping in aramid/epoxy micro-composites. Composites 24(8):635-642.

composites, but it can result in a significant reduction in strength. This combination has proven to be successful in composite armor.[13]

What is clear from prior work is that control over the interface is important not only for protecting fibers, but for controlling properties. In light of this, some areas of interface development are important for improving composite performance.

There are some specialized needs for better sizings for carbon fiber. This includes sizings for vinyl ester resins and, in particular, sizings for carbon-vinyl ester composites of interest to the Navy for topside ship structures. Vinyl ester resins offer significant processing advantage and affordability over bisphenol-based resins. Recent work has shown that thermoplastic sizings of polyhydroxyethers lead to improved processing, improved fiber durability during handling, and improved composite properties in a vinyl ester-based resin.[14] Therefore, it is clear that there are sizing materials that will lead to improved composite properties. Further work in this area is warranted.

Higher-temperature sizings are required that do not degrade in use. As the use temperatures for composites continue to increase, the stability of the interface at high temperature is required to maintain composite performance. Although some work has been done in this area—namely the use of LaRC PETI-5, a phenylethynyl-terminated imide oligomer, as well as some proprietary resins—this is an area in need of some focus.[15,16]

The role of the interface in controlling properties is still not fully understood, particularly as it applies to lifetime prediction, and a better understanding is needed. The interface has a significant effect on fatigue behavior, creep, and environmental stability, yet direct inclusion of interface properties into lifetime models is still under development.[17] To complicate matters further, the interface variability is also a relevant parameter and can lead, for example, to enhanced toughness.[18] One opportunity for improving the cost-effectiveness of composites is tighter design criteria, and this requires—in addition to an understanding of matrix and fiber effects—a thorough understanding of the role of interface variability on composite properties.

The vision for the future should be one in which the fiber properties, matrix properties, and interface properties as well as the stochastic aspects are included in lifetime prediction models that have the confidence of composite designers. In a very ideal future, their performance is monitored in service conditions and data are added back into computer-aided design and computer-aided engineering (CAD/CAE) models to validate and improve their predictive properties.[19-21]

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[13] M. Tanoglu, S.H. McKnight, G.R. Palmese, and J.W. Gillespie, Jr. 2001. Effects of glass fiber sizings on the strength and energy absorption of the fiber/matrix interphase under high loading rates. Composites Science and Technology 61(2):205-220.

[14] J.J. Lesko, J.S.Riffle, N.S. Broyles, N. Verghese, and S.V. Davis. 2000. Composites of thermosetting resins and carbon fibers having polyhydroxyether sizings. U.S. Patent No. 6,020,063.

[15] D. Cho and L.T. Drzal. 2000. Characterization, properties, and processing of LaRC PETI-5 as a high-temperature sizing material. II. Thermal characterization. J. Appl. Poly. Sci. 75(10)1278-1287.

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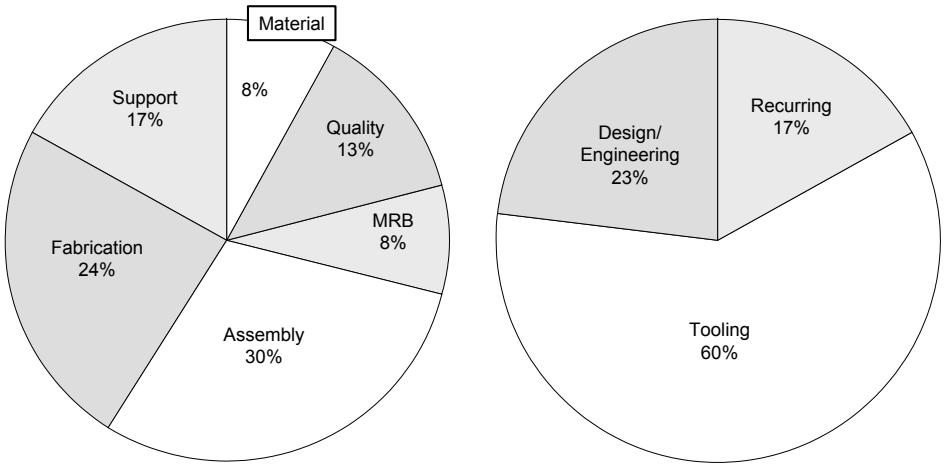
[18] T.U. Marston, A.G. Atkins, and D.K Felbeck. 1974. Interfacial fracture energy and the toughness of composites. J. Materials Science 9:447-455.

[19] Advanced Insertion of Materials (AIM) Program. 2004. Available at http://www.darpa.mil/dso/thrust/matdev/aim/index.html. Accessed March 2005.

[20] G.L. Hahn, K.M. Nelson, and C.R. Saff. 2002. Accelerated Insertion of Materials–Composites. Presented at the 34th International Society for the Advancement of Material and Process Engineering (SAMPE) Technical Conference.

[21] Materials Engineering for Affordable New Systems (MEANS) Program. Available at http://www.afosr.af.mil/pdfs/Hartley/MEANSInfo.pdf. Accessed March 2005.




(a) Recurring Production (F/A 18, AV-8B, F-15)

(b) Prototype Production (2 to 4 aircraft; X-29, X-31)

FIGURE 2.3 Manufacturing costs are substantially higher than materials costs for aerospace composite structures.

## COMPOSITE SYSTEMS

Future DoD systems must become more affordable. The service life of several key tactical aircraft can be measured in decades. For example, the Navy's F/A-18A/B became operational in 1983. The F/A-18C/D was first delivered in September 1987. The F-15 entered the Air Force inventory in 1975; all of these are still in service today The EA-6B, a 1970s-era electronic warfare platform, is slated to remain operational through 2015. Consequently, acquisition and life-cycle costs will have to decrease for future systems. Composite structures offer the potential to last longer and require minimal maintenance.

Future DoD applications will also require a new class of multifunctional materials. The Future Combat System, next-generation ship structures, and unmanned aircraft are some examples of programs where lightweight structure, ballistics, shock attenuation, radar signature reduction, power generation, and embedded sensors and actuators will be needed. Composites provide the opportunity to integrate these functions into a single material system. Affordable processes and robust design methods will be needed to develop and optimize these multifunctional composite materials.

### *Processing*

The acquisition costs for a composite part are comprised of numerous factors including design aspects as well as the costs of raw materials, processing, tooling, assembly, and inspection. Manufacturing and assembly costs have traditionally been significant cost drivers and are typically greater than material costs in aircraft structures (see Figure 2.3). The selection of the process dictates the capital equipment required. The influence of capital equipment costs on final part cost is strongly dependent on the number of parts produced. There are many opportunities for DoD to reduce the cost per part based on the processing methods selected.

Autoclave and automated tow placement (ATP) of prepreg materials and resin transfer molding are commonly used for aerospace applications where performance is the key driver. The robotic ATP process has been shown to dramatically lower costs and improve quality and performance over hand-layup techniques. Manufacturing and assembly costs remain the most significant cost drivers for these applications. Pultrusion, VARTM, and e-beam curing are being evaluated against requirements as alternative lower-cost processes.

One opportunity for reducing composite processing costs is through e-beam curing of resins at room temperature. E-beam curing is a nonthermal process that uses high-energy electrons and/or X-rays to initiate polymerization and cross-linking reactions at controlled rates. The advantages are numerous

and include the following:

- Curing at ambient temperatures, which reduces dimensional changes and internal stresses in the finished product,
- Lower-cost tooling,
- Reduced curing times and continuous operation, and
- Improved resin stability (resins do not have to be stored at low temperature and have extended shelf-life).

The primary challenges facing the current state-of-the-art e-beam resins are the lack of toughness, hot-wet operating temperature limits, consolidation rheology, cost of e-beam equipment, and the general perception of safety concerns. Long-term durability of composites may require optimization of the fiber-matrix interface that forms during e-beam processing.

The needs of the Navy ship, Army ground vehicle, and infrastructure applications are quite different from the needs of aerospace applications. For many of these applications, material costs can become a cost driver. Non-autoclave processes and low-temperature-cure resins are required for large-scale composite structures such as vehicle hulls, ship masts and other topside structures, as well as for bridges, docks, and piers. Affordability is more critical for these applications, with desired costs in the range of $10 to $30 per pound of fabricated structure. The emergence of lower-cost commercial carbon fiber in the range of $6 to $10/lb is now allowing DoD to consider carbon fiber as a cost-competitive alternative to S2-glass. The higher specific properties offered by carbon fiber may even be cost competitive with certain E-glass applications.

Fiber-reinforced polymer matrix composites are becoming increasingly important in many applications such as bridges and highways, off-shore oil platforms, and piers for both new construction and rehabilitation of existing infrastructure.[22,23] In many applications, such as steel girder and concrete rehabilitation, commercially available carbon fiber is the material of choice. In these applications, the service temperatures are relatively low and the matrix must be low cost (polyester, vinyl ester, or phenolic), cure at room temperature, and be available in large volume. In rehabilitation applications, low-cost prepreg and hand-layup, pultrusion of reinforcing strips and secondary bonding, filament winding, and VARTM are examples of typical fabrication processes. For bridge decks, pultrusion and VARTM of polyester and vinyl ester have been demonstrated successfully using glass fiber preforms.[24] Substitution of commercially available carbon fiber for glass in these stiffness-critical applications is a possibility, but the durability of the bond between the carbon fiber and the vinyl ester matrix must be improved. The issue of long-term durability is especially important in these applications, which have lifetime requirements of 30 to 75 years. DoD has a huge infrastructure of piers and docks in need of rehabilitation and should leverage materials and process technologies being developed for civilian infrastructure applications.

A current trend across the industry is the assessment of VARTM to replace more costly processes. As mentioned earlier, ship, ground vehicle, and infrastructure applications currently use this processing technology. However, advancements in resin formulations to improve fire, smoke, and toxicity properties, while retaining the desirable attributes of low viscosity and room temperature cure, are needed. To meet the needs of aerospace, VARTM resins must not only be processible under vacuum pressure (RTM uses much higher positive pressure), but also deliver acceptable structural performance, including mechanical properties and geometric tolerances. Advancement in toughened VARTM resins is needed, and the new

[22] J.W. Gillespie, Jr., D.R. Mertz, W.M. Edberg, N. Nouredine, K. Kasai, and I.C. Hodgson. 1996. Rehabilitation of steel bridge girders through application of composite materials. International SAMPE Technical Conference 28, pp. 1249-1257.

[23] H.V.S. GangaRao and E. Barbero. 1991. Construction, structural applications. Int. Encyclopedia Composites 6:173-185.

[24] P. Cassity, D. Richards, and J.W. Gillespie, Jr. 2002. A "Compositely Acting" FRP Deck and Girder System, High Performance Materials in Bridges and Buildings Conference, Kona, Hawaii, July 29-August 3, 2001 (also published in Structural Engineering International, May 2002).

class of low-viscosity cyclic thermoplastics that polymerize after infusion offers the potential for improved toughness.[25]

Cost studies conducted for the Composites Armored Vehicle Advanced Technology Demonstrator concluded that VARTM offers significant cost savings over the ATP process for multifunctional materials such as integral armor hull structure (hybrid construction consisting of signature layer, alumina ceramics, and polymer matrix composites) at a cost of $30 to $40 per pound.[26] In addition, VARTM has been the process of choice for fabrication of large-scale ship prototype structures. VARTM processing of low-permeability carbon preforms for topside structures is in the early stages of development.

The VARTM process is also being evaluated critically for aerospace applications as an alternative to RTM. VARTM is a low-pressure process that offers reduced tooling costs. Fiber volume fractions and associated properties are lower than those of higher-pressure processes such as RTM and autoclave. Parts may have to be redesigned and may add weight. The process uses one-sided tooling, and strict control of geometry is not yet possible and may add to assembly costs. Advances in preform technologies may allow for improved properties and dimensional tolerances. Future studies should consider these cost-performance trade-offs.

Virtual manufacturing and simulation should play an increasingly important role for accelerated insertion of materials and processes into DoD systems. In the case of VARTM, advancements in intelligent processing will allow for risk and cost reduction but require advancements in three-dimensional flow simulation in porous media as well as models to predict input properties such as the permeability tensor as a function of fiber architecture, compaction, and distortion.

In summary, VARTM is being considered by all services as an affordable process. However, it is largely a manual process. Research in automation using simulation, sensing, and control systems should be pursued to advance this process from prototype to a production-ready process.

### *Translation of Fiber Properties to Composite Properties*

Precisely how the distribution of individual fiber strengths affects the reliability of a composite structure containing billions of continuous fibers is an extremely important question. This issue was noted in the earlier discussion of large-tow strength distributions versus those from small tows. The effect of fiber property variability on design allowables for composite structures must be understood in order to take advantage of incremental improvements in small-tow SAF fibers to achieve weight reduction in legacy systems and to effectively use textile fiber processing that may offer significant cost savings. Although stiffness is important, certification of a detailed design will depend on an accurate strength analysis of the problem. Simply stated, if the individual fiber strength distribution is known, can one predict how this will be translated into a composite tow, then into a fabric consisting of many tows, then into a multilayer laminate, and finally into a composite structure?[27] Verification of this approach remains to be done, but the ramifications, if it is successful, are very far reaching for aerospace, commercial, and DoD structural applications.

Precise control of fiber orientation is needed during processing to achieve full translation of the fiber properties into the composite. In high-modulus fibers such as carbon and organic fibers, a misorientation of only 5 degrees in a unidirectional material can cause a modulus drop of 15 to 25 percent (depending on the fiber volume loading) for a carbon-epoxy composite.[28] Preimpregnated fabrics are also commonly used in many applications. These systems are typically two-dimensional weaves of fibers ranging from 1k to 24k in a variety of patterns that offer different ranges of properties in orthogonal directions (e.g., plain weave, 5-harness satin, 8-harness satin, etc.). In other applications, such as RTM and VARTM, the fiber tows are woven dry, placed in a tool, and impregnated with resin.

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[25] J.W. Gillespie, Jr., D.A. Eckel II, W.M. Edberg, S.A. Sabol, D.R. Mertz, M.J. Chajes, H.W. Shenton III, C. Hu, M. Chaudhri, A. Faqiri, and J. Soneji. 2000. Bridge 1-351 Over Muddy Run: Design, Testing and Erection of an All-Composite Bridge. Transportation Research Record 1696:118-123.

[26] Composite Armored Vehicle Advanced Technology Demonstrator Design Guide. 1999. Contract DAAE07-94-C-R011. U.S. Army TACOM.

[27] E.M. Wu and C.S. Robinson. 1998. Computational micro-mechanics for probabilistic failure of fiber composites in tension. Composites Science and Technology 58:1421-1432.

[28] S.W. Tsai and H.T. Hahn. 1980. Introduction to Composite Materials. Lancaster, Pa.: Technomic Publishing.

Preform technologies are advancing with an almost unlimited degree of freedom to orient fiber tows in three dimensions and weave them to near net shape. Advanced three-dimensional preforms offer increased stiffness and strength in the through-thickness direction (at the expense of in-plane properties), improved damage tolerance, and potential for improved ballistic performance for composite armor.

Mechanical property models exist for the prediction of thermoelastic properties of these various fiber architectures. However, the ability to predict damage evolution and long-term durability is not sufficiently robust and is currently dependent on expensive testing programs. Future research should be directed toward establishing reliable models to relate fiber, matrix, and interface properties, processing effects, and fiber architecture to damage mechanisms and life prediction.

## FIBER QUALIFICATION COST ISSUES

Historically, the development of structural fibers has been driven by two competing factors: performance and cost. In general, fibers with higher strength and modulus are more expensive than fibers with more moderate properties. Early in the development of structural fibers, the selection of a fiber for a particular application—especially a military application—was driven primarily by performance requirements. With the emergence of non-aerospace, non-military applications, cost—given an acceptable level of performance—has become the driver for fiber selection. Cost has also become a major concern of DoD when making material selections for future military applications. Despite this concern about cost, however, DoD continues to require a high degree of fiber consistency. Demonstration of this consistency (by the fiber producer) drives up material costs.

There are several important factors controlling fiber cost: the cost of the raw material; processing costs; and—for military applications—the cost of qualifying a material for a given application, including the quality control and reporting that are required for fibers to meet military specifications. Commercially available fibers do not have this third cost and, as a result, are significantly cheaper.

It is important to recognize that material costs, and specifically fiber costs, are just one factor affecting the cost of a composite part. The recurring costs associated with composite processing, component assembly, and product inspection can be significant. In some applications, material costs are a small fraction of the total cost of the system. In addition, nonrecurring costs may be related to material qualification of the fiber, of the resin, and of the fiber and resin combination in the composite, at both the coupon and the structural levels.

The magnitudes of composite material and component qualification or certification efforts and costs vary widely and depend on many factors, including specific product requirements, the criticality of the application, and the degree to which human safety is involved. In military aircraft, for example, the process of design development, material qualification, process development, structural analysis, and testing can be extremely complex and costly due to mission criticality, the need for high reliability under extreme conditions, and survivability requirements. With increasingly stringent requirements and more sophisticated composite products, qualification and certification programs have become more and more complex over the years, and with this complexity has come increased cost. Therefore, if new materials have only marginal (though desirable) benefits compared to existing systems, end users may be unwilling to expend the resources necessary to qualify them if qualification costs remain at present levels. Conversely, for DoD to take advantage of incremental improvements in current fibers or lower-cost commercial fibers, more efficient approaches to material qualification will be needed.

## COMPOSITES AS SYSTEMS

In the past, research on composites has been viewed as a collection of issues, such as fiber development, matrix studies, interfacial bonding, processing, and finally structural mechanics. Traditionally, matrices have been thought to protect the fibers. However, it is now understood that the matrix will influence the entirety of process-structure-property relationships for the composite system while leaving the fibers unchanged. Further, the properties and structure of the resin matrix are different when reinforced, and this presents a major challenge. Only recently has the industry matured to the point where the fiber, resin matrix, interface, and surface are routinely seen as a system.

With the development of computers capable of modeling structures at the molecular scale, the time is approaching when it will be possible to design the optimum composite for a given system performance and cost. This systems perspective will involve modeling the structure and the manufacturing processes

at various length scales to relate microstructural behavior to system performance. This modeling will include the placement of the reinforcing phase, the structure of the matrix phase, and even the degree of bonding at the interface. The methodology could be used to predict (and even control) the final structure of the composite. In other words, future engineers will not merely analyze the mechanics of the final product, but will apply a systems perspective and employ advanced modeling techniques to create reinforced structures that best meet given system requirements. This approach is the key to reduced cost and accelerated insertion of new materials into DoD systems.[29-32]

A systems approach is also crucial to understanding the stochastic aspects of composite failure, which is essential for improving the design criteria of these systems. Lack of knowledge in this regard can lead to excessive design safety margins that result in increased weight and cost and lower system performance. A better understanding of the effect of constituent variability on composite properties is crucial to taking advantage of fibers on the market today as well as future fibers, as is the development of micromechanical and continuum-based models that include the stochastic process for the prediction of composite behavior.

The transition to a systems approach is likely to occur gradually, with full implementation 10 or more years in the future. While this approach is evolving, researchers and material suppliers will continue to make incremental improvements in reinforcing fibers, matrix resins, and composite forms and processes.

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[29] G.L. Hahn, K.M. Nelson, and C.R. Saff. 2002. Accelerated Insertion of Materials—Composites. 34th International Society for the Advancement of Material and Process Engineering (SAMPE) Technical Conference.

[30] G. Havskjold, Materials and Manufacturing Directorate, Air Force Research Laboratory. 2000. Robust Design Computational System. AFRL-ML-WP-TR-2000-4093. April.

[31] National Research Council. 2004. Accelerating Technology Transition. Washington, D.C.: National Academies Press.

[32] Advanced Insertion of Materials (AIM) Program: Available at http://www.darpa.mil/dso/thrust/matdev/aim/index.html. Accessed March 2005.

# 3

# The High-Performance Fiber Industries

The carbon and high-performance organic fiber industries have developed from the 1960s to the present. An understanding of their history is important to understanding the future of these highly volatile industries.

## THE CARBON FIBER INDUSTRY

### *1969 to 1989—The First 20 Years*

High-strength carbon fiber came out of the development laboratories in Japan, England, and the United States in the late 1960s. The initial fibers were very expensive (more than $400 per pound), but in the early 1970s, continuous processes were developed and the cost declined steadily over the next decade. The Air Force Materials Laboratory took the lead in U.S. government-sponsored material development and hardware demonstration. By the late 1970s, materials were used in the production of primary structures for military aircraft and missiles. These applications were followed by selective use in commercial aircraft.

For 20 years, between 1969 and 1989, the carbon fiber industry had phenomenal technological success and double-digit annual growth in aerospace and defense, with additional use in sports equipment and some limited use in automotive and industrial applications. This growth attracted many large international companies into the industry. The vision was that continued growth in military and commercial aircraft use would be followed by a very large industrial market by the year 2000. However the engine that had powered this success, the U.S. Department of Defense, had stalled.

During this period, usage by DoD peaked in 1989, and in 1990—with the collapse of the U.S.S.R. and the end of the Cold War—and after 20 years of growth, the DoD market started to decline. In 1990, DoD usage was only 40 percent of what it was in 1989. Figure 3.1 shows the U.S. carbon fiber usage from 1981 for DoD and non-DoD applications. Table 3.1 shows that the cumulative usage for DoD between 1991 and 1995 based on the 1991 forecast, was down 78 percent from 1987 projections.

These forecasts made in the late 1980s, driven by DoD demand, were the justification for major capacity expansions around the world. Table 3.1 shows that as a result of these perceived market opportunities, worldwide carbon fiber production capacity increased by 45 percent from 1989 to 1990.

In 1985, after several years of study based on continuing assessment of weapons system production needs for composite materials, the Department of Defense was found to be unacceptably dependent on foreign industry for PAN-based (polyacrylonitrile-based) carbon fiber. Virtually all military aircraft, current and prospective generations of strategic missiles, and certain spacecraft were expected to use composite materials in some form. Defense production requirements for PAN-based carbon fiber were projected to increase dramatically in the foreseeable future. However, there were no domestic PAN-based carbon fiber sources qualified at that time for use in military systems. Because classified programs were also dependent on foreign industrial sources of PAN-based carbon fiber to achieve time-critical missions, the potential for supply denial, even under peacetime conditions, was unacceptable. In

TABLE 3.1 DoD Carbon Fiber Usage (millions of pounds)

| | 1991 | 1992 | 1993 | 1994 | 1995 | Cumulative |
|---|---|---|---|---|---|---|
| 1987 forecast | 4.84 | 6.09 | 7.09 | 6.97 | 6.67 | 31.66 |
| Actual | 0.95 | 1.10 | 1.30 | 1.64 | 1.86 | 6.85 |
| Reduction | 3.89 | 4.99 | 5.79 | 5.33 | 4.81 | 24.81[a] |

[a] Down from 1987 forecast by 78 percent

December 1987 Congress passed Public Law 100-202 directing the Secretary of Defense to ensure that a minimum of 50 percent of the PAN precursor for carbon fibers would be procured from domestic sources by 1992 provided that 15 percent was procured from domestic sources by 1988-1989, 20 percent by 1990, and 25 percent by 1991.

The Department of Defense implemented the law through a policy memorandum and two Defense Federal Acquisition Regulation Supplement (DFARS) clauses. In July 1999, the Under Secretary of Defense for Acquisition issued a policy memorandum directing military departments to use 100 percent domestic PAN on all major weapons that had not yet entered production. This legislation is still in force today.

In 1989, after 20 years of development, approximately 40 percent of the global market was concentrated in the United States. In Japan, Taiwan, and Korea, the total usage was approximately equal to that of the United States, but it was predominantly for sports equipment. However, there were emerging developments in automotive and industrial markets in Japan. The European market was about one-half the size of the U.S. market and was predominantly commercial aircraft.

The carbon fiber industry entered the 1990s with a major overcapacity condition, demand less than one-half capacity, and a declining U.S. DoD market.

### *1990 to Present*

The worldwide overcapacity and decline in the DoD market led to major reductions in carbon fiber prices and renewed application development. In 1990, DoD usage was at about 1 million pounds annually and no major growth was predicted. The industry strategy was to broaden commercial aircraft use, develop the sports equipment market, and seek industrial applications.

Starting in 1995 there was major industry consolidation:

- 1995—Hexcel merges with Ciba Composites,
- 1998—Hercules sells carbon fiber and prepreg business to Hexcel,

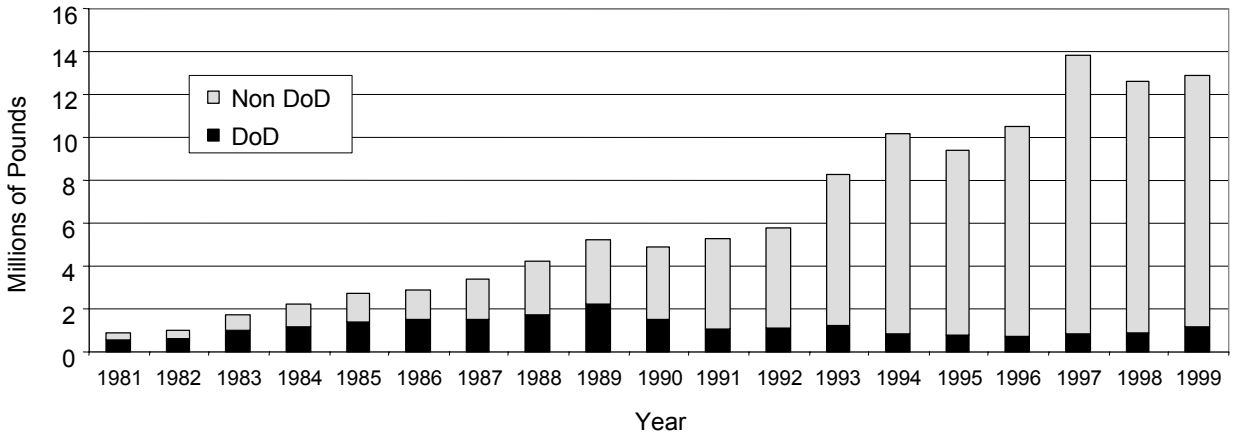


FIGURE 3.1. Carbon fiber use in the United States. DATA SOURCE: Suppliers of Advanced Composites Materials Association (SACMA). 1999. Unpublished data provided to the committee prior to the dissolution of the organization.

TABLE 3.2 Worldwide Advanced Composite Carbon Fiber Shipments for 1992-1997

| Year | Pounds | U.S. Dollars |
|---|---|---|
| 1992 | 13,002,812 | 374,100,000 |
| 1993 | 14,598,544 | 384,900,000 |
| 1994 | 17,423,452 | 461,400,000 |
| 1995 | 19,714,671 | 489,240,000 |
| 1996 | 20,672,741 | 469,240,000 |
| 1997 | 25,964,530 | 621,410,000 |

SOURCE: Suppliers of Advanced Composite Materials Association (SACMA). 1999. Unpublished data provided to the committee prior to the dissolution of the organization.

- 1997—R.K. Textiles sells carbon fiber business to SGL,
- 1997—DuPont sells advanced composites business to Fiberite,
- 1997—Fiberite sells prepreg business to CYTEC,
- 2001—BP Amoco sells carbon fiber business to CYTEC, and
- 2004—Toho Tenax announces plans to acquire Fortafil Fibers to establish domestic manufacturing base.

In 1997, Suppliers of Advanced Composite Materials Association (SACMA) carbon fiber statistics (Table 3.2) showed that world carbon consumption had reached 26 million pounds.[1] Modest expansions in capacity had been made in the 1990s, bringing the world capacity to approximately 26 million pounds (considering product mix). In the 1990s there was also renewed interest in carbon fiber manufactured from large commercially available tows in an attempt to lower the cost.

Analysis of the 1997 SACMA data shows the following:

- Consumption in 1997 was 26 million pounds, more than 5 million pounds greater than in 1996, a better than 25 percent increase—the largest increase in the history of carbon fiber;
- DoD usage was up 55 percent over 1996 reaching 1.3 million pounds, representing 9 percent of the U.S. market and 5 percent of the world market;
- Commercial aerospace usage was 4.7 million pounds, up 2.8 million pounds over 1996, or a 77 percent increase;
- Commercial aerospace usage was 6.5 million pounds, or 25 percent of the total market;
- Worldwide sports equipment usage was 9 million pounds, or 35 percent of the total market;
- Worldwide industrial usage was 31 percent of the total market;
- Worldwide automotive usage was 4 percent of the total market; and
- U.S. consumption was 55 percent of total market.

From 1994 to 1997, the growth in the commercial aerospace market, the sporting equipment market, and the industrial markets created a much-improved scenario for the carbon fiber industry. In 1997, the industry was at capacity, carbon fiber was in very short supply, and the bottom line for most carbon fiber manufacturers was healthy. To cope with the fiber shortfall, all of the major carbon fiber manufacturers expanded their capacities. The projected world carbon fiber capacity by 1999 was expected to be approaching 50 million pounds, again leaving demand less than one-half of capacity.

[1] Suppliers of Advanced Composites Materials Association (SACMA). 1999. Unpublished data provided to the committee prior to the dissolution of the organization.

In 1999 the industry experienced another slowdown in the major markets:

- A major slowdown in the sporting goods market,
- A major slowdown in the use of chopped carbon in molding compounds,
- Reduction of personnel in major prepreg and carbon fiber companies, and
- Boeing commercial aircraft deliveries peaking in 1999 at 620; forecasted deliveries for 2000 were for 480 aircraft.

The second feast and famine cycle had started again at an overall market growth rate of 10 percent; supply would exceed demand for nearly 5 years.

The forecasted growth did occur. At the beginning of 2004, the industry was again at capacity for carbon fiber manufactured from SAF precursor. Major growth has occurred in industrial markets and in use by Airbus, starting with the development of the A380. The forecasted delivery of 40 aircraft per year and 58,000 pounds of carbon fiber per aircraft would represent a demand for 2.2 million pounds of carbon fiber per year. Boeing is also planning a new aircraft that is estimated to use 50 percent carbon composites.[2] The wind energy industry, established for more than 30 years, is showing some renewed interest in carbon fiber, especially in Europe for large wind turbine blades. The offshore oil industry is testing some prototype carbon composite structures. To meet this rising demand, Toray has completed a 4-million-pound expansion, and another 4-million-pound increase in capacity is under way, with half of this capacity established in U.S. operations.

In the United States, the number of unmanned air vehicles and the use of carbon fiber composites are growing. The surface Navy has been actively developing composites with a focus on fiberglass. However, the Navy is now showing interest in carbon for proposed new programs such as DD(X) and the littoral combat ship. This interest in carbon fiber has accelerated because of the carbon composite Visby corvette developed by Kockums AB and the Swedish Navy. These DoD applications should take advantage of lower-cost, commercially available carbon fibers developed for commercial markets. Based on the stated program requirements, current fiber properties will meet the needs of these programs.

*Trends in Pitch- and Rayon-based Carbon Fibers*

The nameplate worldwide production capacity[3] for pitch-based carbon fiber in 2004 was about 6.3 million pounds, compared with about 73.5 million pounds for PAN-based carbon fiber (both small and large tow), as shown in Table 3.3. Official figures of actual demand for pitch-based carbon fiber were not available, but in 1999, it was estimated that the demand for these fibers was on the order of thousands of pounds, rather than millions of pounds.[4] There will likely be an increased demand for pitch-based carbon fibers in the future to satisfy the needs of thermostructural applications. In the United States, the demand for pitch-based fibers is limited to carbon-carbon brake applications, which were initiated in the 1970s, and limited thermal management applications in satellites and aerospace applications.

ConocoPhillips built an 8 million-pound-per-year capacity manufacturing plant for pitch-based fiber that was scheduled to begin production in 2002.[5] The process used a melt-blowing technique to convert a “solvated” mesophase pitch into a randomly oriented fiber mat. In this type of process the precursor is melted and extruded from a spinneret. At the point of extrusion, a high-velocity gas stream, flowing nearly parallel to the extrudate, draws and quenches the filament. The solvent in the ConocoPhilllips precursor was rapidly dried in the first stages of stabilization, yielding a discontinuous mesophase pitch fiber with a relatively high melting point (around 400°C). This allowed the fiber mat to be stabilized at a higher temperature, greatly reducing the time needed for this step of the process. As a result, the ConocoPhillips process was continuous from melt spinning through carbonization. The goal was to produce a high-modulus, intermediate-strength, discontinuous pitch fiber for a wide range of applications

[2] Boeing press release, July 2004.

[3] An official, publicly disclosed, maximum annual production volume of product produced by a plant.

[4] F.T. Traceski. 1999. Assessing industrial capabilities for carbon fiber production. Acquisition Review Quarterly 6(2):179-189.

[5] Conoco Annual Report. 2001.

such as electronics, automotive brakes, and infrastructure. However, a failure to meet market expectations caused management to shut down the process and dispose of the equipment.

Demand for rayon-based fibers varied between 100,000 and 1 million pounds (45,000 and 450,000 kg) in the 1990s depending on fluctuations in stockpiling and use by the Department of Defense (DoD) and National Aeronautics and Space Administration (NASA). There has been no immediate demand for new rayon production designated for aerospace use, and there is no longer a qualified domestic source of these fibers.[6]

### *Observations on History*

The carbon fiber industry has experienced significant growth over the past 30 years, reaching a worldwide market of more than 40 million pounds in 2004. Significant improvements were made in fiber properties, and major cost reductions have been achieved. Carbon fiber prices based on SAF precursor have fluctuated with capacity and market conditions. The price of standard-modulus (32 Mpsi) SAF carbon fiber reached an all-time low of $5.25 per pound in 2003. The emergence of affordable SAF carbon fiber with less variability in properties represents significant competition for textile-based carbon fiber in commercial and DoD applications. Table 3.3 describes the current production capacity.

In the United States, none of the original manufacturers of carbon fiber was able to achieve the desired returns, and each exited the business. A number of companies have invested in the promise of high-strength carbon fiber; many of them are no longer in operation. Courtaulds in the United Kingdom ceased carbon fiber production in 1991, while Hercules sold its carbon fiber plant to Hexcel in 1996. The original Union Carbide carbon fiber operation is now owned by Cytec—after being part of AMOCO and British Petroleum.

The original Japanese companies—Toray, Toho, and Mitsubishi—all have substantial market shares in PAN and are still major participants. These three companies today represent almost 80 percent of the stated worldwide capacity for SAF-based carbon fiber. As of mid-2004, two Japanese companies had announced expansion plans. Toray will add 4 million pounds of new capacity at its Soficar plant in France in 2004 and 4 million pounds of carbon fiber capacity at its plant in Decatur, Alabama, along with the precursor capacity to support this expansion. Toho has also announced an additional 1,500-tonne expansion in Germany.

Without a special relationship with a large local market—such as the U.S. Department of Defense—success in the manufacture of an internationally traded material such as carbon fiber depends on achieving competitive quality and price. Toray's consistent investment in process technology improvements has enabled it to become the world leader in carbon fiber production. This has been achieved, despite periods of negligible profitability, because of the characteristics of the Japanese innovation system.[7]

In summary, the committee made the following observations:

- In 2003, DoD accounted for approximately 4 percent of total world carbon fiber usage.
- DoD has stated that the properties of available carbon fibers meet all of its current needs.
- Any impact of the new technology on low-cost carbon fibers is at least 10 years away.
- There is adequate installed capacity in North America to supply DoD needs for the next 10 years.
- Near-term shortage of SAF carbon fibers will have no significant impact on DoD.
- In cases where DoD is using a sole source, it often encourages a second supplier to develop an equivalent product.
- Modifications in the specification requirements that ensure the measurement of necessary features while reducing the number of tests and the cost of testing would be desirable.

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6 Traceski, 1999. See note 4 above.

7 G. Spinardi. 2002. Industrial exploitation of carbon fibre in the UK, USA, and Japan. Technology Analysis and Strategic Management 14:381-398.

TABLE 3.3 Worldwide Pan-Based Carbon Fiber Capacities at the End of 2004 (millions of pounds)

| | Company | Plant Location | Nameplate Capacity[a] |
|---|---|---|---|
| SAF tow | Toray | Japan | 10.4 |
| | | Germany | 5.8 |
| | | United States | 4.0 |
| | Toho | Japan | 8.2 |
| | | Germany | 4.2 |
| | Mitsubishi | Japan | 7.0 |
| | | United States | 3.3 |
| | Hexcel | United States | 4.4 |
| | Cytec | United States | 4.2 |
| | Formosa | Taiwan | 3.9 |
| Total SAF | | | 55.4[b] |
| Textile tow | Toho | United States | 7.7 |
| | Aldila | United States | 2.2 |
| | SGL (Sigri) | Scotland | 4.2 |
| | Zoltek | United States | 4.0 |
| Total textile | | | 18.1 |
| Combined total | | | 73.5 |

[a] Estimated 12k equivalent nameplate capacity

[b] This total reflects an estimated 78 percent ownership of world SAF capacity by Japanese companies.

SOURCE: Intertech. 2004. The Global Outlook for Carbon Fiber. Proceedings of a conference in Hamburg, Germany, October 18-20. Portland, Me.: Intertech Corporation.

- New SAF capacity for commercial applications will provide an alternate source of affordable carbon fibers for DoD systems.

## THE ORGANIC FIBER INDUSTRY

### *Historical Development*

The high-performance organic fiber industry began with the commercial introduction of the *m*-aramid fiber Nomex in the late 1960s. It major applications included thermal and flame protection.

Since then, several classes of fibers have been commercialized: high-strength *p*-aramid fibers in the early 1970s; liquid crystalline polyester (LCP); ultrahigh-molecular-weight polyethylene (UHMWPE); and poly (*p*-phenylene-2,6-benzobisoxazole) (PBO) in 1990s. The most recent addition is M5® fiber, which is in the final stages of development.

Like the carbon fiber industry, developments in organic fiber technology during the 1970s and 1980s enabled the use of lightweight polymer-matrix composites in military and commercial applications. Unlike the carbon fiber industry, however, growth in the high-performance organic fiber industry was driven from the beginning by a combination of military and commercial, aerospace and non-aerospace applications. The unusual combination of mechanical, thermal, flame, and other properties found in most of the high-performance organic fibers, as well as the ability to tailor these properties to specific needs, has enabled this wide range of applications.

#### *Demand for High-Performance Organic Fibers*

Demand for high-performance organic fibers grew steadily from the late 1970s to the mid-1990s due to the large number of commercial applications. Between 1980 and 1995, the rate of growth in

consumption volume for *p*-aramids and *m*-aramids reached 6 to 7 percent. These two fiber types represent more than 90 percent of worldwide demand for high-performance organic fibers and can therefore be used as a good approximation of general consumption trends. By 2002, the demand for *p*-aramid alone had risen to approximately 90 million pounds, more than two times the demand for PAN-based carbon fiber.[8]

*Production Capacity and Price for High-Performance Organic Fibers*

In the mid-1990s, substantial production capacity existed for high-performance organic fibers in the United States, Europe, and Japan. Worldwide production capacity in 1994 was estimated to be approximately 132 million pounds, with the largest capacity (72 million pounds) located in the United States.[9] *p*-Aramid fibers accounted for the largest production capacity (89 million pounds), followed by *m*-aramids (36.1 million pounds), UHMPEs (approximately 5 million pounds), LCPs (approximately 1.1 million pounds), and PBOs (0.4 million pounds).

### *Current Status and Trends of the Organic Fiber Industry*

The high-performance organic fiber industry has grown steadily in recent decades. From the beginning, the industry's dependence on high-volume commercial applications, rather than DoD applications, has contributed to this stability. Demand for high-performance organic fibers remains high, as a result of their broad range of applications, and there is potential for future growth. Installed production capacity is significantly larger than that for carbon fibers, and although it was adequate to meet the needs in the past, the committee sees indications of reaching the limits of existing capacity. New applications that are being developed will be able to take advantage of incremental increases in existing production capabilities but should anticipate major investment decisions in this industry in the next 5 to 10 years. The continuing tailoring of products to applications leads to a fragmentation of existing production capability, and thus, analysis of total capacity may result in misleading conclusions.

In the case of high-performance organic fibers, developments will continue to be driven by the commercial sector. DoD represents a small portion of the total organic fiber market, but an important one for products tailored to its applications. As such, DoD may be able to continue to take advantage of the base created by commercially driven developments, but it will have to take its specialized uses into account. Future DoD usage will likely have a significant impact on the development and commercialization of the new fiber, M5.

### *Investments Plans Announced in 2004 by DuPont and Honeywell*

DuPont has disclosed plans to expand production of its high-performance DuPont Kevlar *p*-aramid. DuPont plans to invest more than $70 million in this project and is beginning the equipment procurement process. The expansion will increase global Kevlar capacity by more than 10 percent. The project is scheduled to come online in phases between late 2005 and the first half of 2006. The specific expansion locations will be finalized as required to meet the projected start-up dates. This is the fourth expansion that DuPont has made in Kevlar *p*-aramid capacity since 2000 due to growing customer demand for this high-strength fiber that supports global safety and performance applications. In addition to these expansions, DuPont continues to increase capacity by optimizing the productivity of existing assets through the use of Six Sigma processes. Between 2000 and 2003, DuPont completed three Kevlar high-performance fiber expansion projects at its Richmond, Virginia, Vancouver, British Columbia, and Maydown, Northern Ireland, facilities. The 2003 expansion and the latest announced expansion both incorporate proprietary New Fiber Technology (NFT) developed and patented by DuPont.

Honeywell announced a $20 million investment to boost production of Spectra fiber to meet increased demand from the North American armor industry. Honeywell expects to make several similar-sized investments in Honeywell Performance Products over the next few years to boost Spectra fiber production. The current investment will take place at Spectra fiber manufacturing facilities in the

[8] D.J. DeLong. 2002. Carbon fiber cost analysis and trends, presentation at the Global Outlook for Carbon Fiber, Raleigh, N.C., October 21-23, 2002.

[9] Chemical Economics Handbook. 1995. Menlo Park, Calif.: SRI Consulting.

Richmond, Virginia, area. This expansion is expected to be completed in the second quarter of 2005. The additional production will be devoted primarily to meeting U.S. military requirements. This Richmond-area build-out is independent of a previously announced Spectra fiber manufacturing operation intended to support the global marketplace. Additional capacity for domestic fiber is also being added by Dyneema.

# 4

# Opportunities for DoD-Sponsored Research

The high-performance fibers that are being used today in DoD applications are the end result of decades of research and development. The PAN-based carbon fibers continue to be produced using fundamental technology developed in the 1960s. The first product among organic fibers, Kevlar, was introduced commercially in 1972. Although the fundamental properties of filaments quoted in the first patents are very close to today's products, the yarn properties have been improved significantly.[1] This trend is continuing and does reflect improvement of commercial processes in both their fundamental design and their control. Both PAN and mesophase pitch carbon fibers have followed similar R&D time lines with both single-filament and bundle properties improving significantly. Given the maturity of these fibers, it seems unlikely that there will be dramatic improvements in fiber properties in the near term (5 to 10 years); rather, the principal R&D opportunities in this period appear to be in efficiently taking advantage of these fiber properties in finished composite structures and in cost reduction.

While the DoD-stated performance of commercially available fibers appears sufficient to meet near-term DoD requirements, they may not meet all the needs of the next-generation systems of 2010 and beyond. For example, as outlined by the Future Combat System (FCS) and Objective Force Warrior initiatives, the protective garment of the future will have to protect a soldier from the full spectrum of threats (ballistic, chemical, biological, environmental) and act as the foundation upon which the soldier's power grid, communication system, and sensor arrays can be built. For the future soldier system to achieve the degree of functionality that will be required in 10 to 15 years, while maintaining or reducing the overall system weight, new multifunctional fiber materials and associated composite systems and processing techniques must be developed, and this development must start now. It can be expected that the development of multifunctional composites for armored vehicles, topside ship structures, and unmanned robotic and aerial vehicles will face similar demands to meet requirements for reduced weight and increased functionality. The creation of such composites will require prudent investment as well as vision on the part of DoD program managers.

In view of this time-differentiated array of research opportunities, this chapter is organized into two major sections: (1) opportunities for incremental performance gains and cost reduction (5 to 10 years) and (2) opportunities for more revolutionary gains (more than 10 years).

## NEAR-TERM (5 TO 10 YEARS) PERFORMANCE GAINS

In projecting what might be expected in terms of gains in fiber performance properties in the future, one must separate incremental gains made using current technology from major leaps arising from new non-PAN precursors and/or completely new fiber technologies. This section discusses near-term expectations that would not require a multiyear development period.

[1] E.I. du Pont de Nemours and Company. Diverse utilization of DuPont Kevlar. Available at http://www1.dupont.com/dupontglobal/corp/documents/US/en_US/news/releases/media/pdf/kevlar.pdf. Accessed March 2005.

### *Carbon Fiber Improvements*

*PAN-Based Fibers*

Today's commercially available PAN-based carbon fibers cover a wide range of properties. The tensile strength ranges from approximately 2.5 to 6.5 GPa (362 to 943 kpsi), while tensile modulus ranges from approximately 220 to nearly 500 GPa (32 to 73 Mpsi). With this broad a product portfolio available, most of the research in the industry is pursuing gains other than improvements in properties. Suppliers of the small-tow carbon fiber (3k to 12k filaments) are working to reduce their costs while maintaining fiber properties. Manufacturers of large-tow fibers (more than 12k and often as much as 320k filaments) are trying to match the performance of the smaller-tow fibers and reduce product variability. Manufacturers of both small- and large-tow carbon fibers are working to improve process control so as to increase process efficiency and improve product uniformity. New monitoring techniques are becoming available that could improve the quality and consistency of both small- and large-tow products. These include high-resolution optical probes for monitoring gels and flaws, portable on-line Raman instruments for monitoring structure, and laser instruments for monitoring fiber size. These and other advanced monitoring techniques are being evaluated on pilot-scale fiber lines in academia and industry.

For PAN-based carbon fiber properties, two important research areas have arisen. First, does a wider distribution of properties such as strength, for example, affect the realizable properties of the final part and, if it does, can this effect be predicted reliably and accommodated in the final composite design? This question is important to both the high-performance aerospace user and the much larger-volume applications for infrastructure, transportation, and energy. The effect of a given proportion of low-strength individual filaments in a tow on the strength of a composite made by impregnating the tow with resin is largely unknown. Further, the effect of the initial filament strength distribution on the strength reliability and lifetime of the impregnated tow and, in turn, on the reliability and lifetime of the final part made from many tows, is also not known. Current lifetime models do not consider the statistics of the failure process. Although a model has been developed to accomplish such a prediction,[2] no databases exist to verify it. Furthermore, such verification would require an integrated study among fiber producers, prepreg and towpreg companies, and composite part manufacturers. In addition, in situ monitoring of composite part integrity and health could be used to validate such models. The successful outcome of such an effort would result in a lower factor of safety needed for a given reliability, as well as the ability to certify very large parts with minimal or no full-scale testing. Both of these advantages would result in very large cost savings.

A second research thrust would be to improve the uniformity of the carbon fiber. For example, reducing the variability in fiber weight per unit length will reduce the fiber areal weight variability in prepreg. Because processing technology is generally tightly held by the companies, some mechanism such as a consortium of universities, government, and companies to produce results useful to all might be a mechanism for achieving this goal.

Long-term opportunities to improve the compressive properties of fibers are more difficult to define. Many designs are limited by the compressive strength of the composite. Research has shown that both intra- and intercrystalline disorder must be increased if the compressive properties in both PAN- and pitch-based carbon fibers are to be improved.

*Pitch-Based Fibers*

Although pitch-based carbon fibers have been around for some time, they have managed to penetrate only some small niche markets. The primary reason is that many applications for carbon fibers to date have been strength-driven. This has given PAN-based carbon fibers, with their less flaw-sensitive nongraphitic structures, a natural advantage. However, because of their graphitic structure, the thermal conductivities of pitch-based carbon fibers are as much as three times that of copper and orders of magnitude higher than those of PAN-based carbon fibers, and applications are now emerging in which heat transfer is critical. For example, management of excess heat has become a limiting factor in the design of many military aircraft, satellite structures, and electronic packages. During high-speed

[2] E.M. Wu and C.S. Robinson. 1998. Computational micro-mechanics for probabilistic failure of fiber composites in tension. Comp. Sci. Tech. 58:1421.

maneuvers, air drag generates significant heat on flight surfaces, limiting aircraft performance. Satellites are exposed to large thermal gradients that cause warping and dimensional changes. The increasing density of the electronics packages aboard aircraft also makes thermal management a critical design issue.

Solutions such as active cooling systems lead to weight penalties and increased system complexity. Passive cooling offers the potential for simplified system designs and reduced weight; pitch-based carbon fiber composites are ideal for these applications. The most promising passive approach consists of using the structure itself (either the airframe or the electronic package) to withdraw excess heat. In this approach, the structure is a composite material reinforced by high-thermal-conductivity, mesophase pitch-based carbon fibers. Applications such as brakes and electronics could create high-volume markets that can be satisfied only by pitch-based carbon fibers. Thus, although pitch-based carbon fibers are unlikely to challenge PAN-based carbon fibers in strength-driven applications any time in the foreseeable future, thermal management may create an even larger market in which pitch-based carbon fibers will dominate. However, for this market to grow, the price of high-thermal-conductivity pitch-based carbon fibers must be reduced significantly.

Promising areas for cost reduction in the pitch process are precursor chemistry and the exploration of parameters that control structure during fiber processing, such as fiber property development related to heat treatment. Recent research has shown that fibers produced using more uniform mesophase precursors can develop extremely high thermal conductivities at lower graphitization temperatures than those currently employed in commercial processes. New analytical techniques such as matrix assisted laser desorption ionization (MALDI) mass spectroscopy allow mixtures of complex organics to be characterized. Based on advances such as this in instrumentation, it is now possible to quantify the composition and, thus, monitor the uniformity of the pitch precursor.

Optimization and control of molecular orientation during fiber formation also allow the fiber to develop high thermal conductivities at lower temperatures. For example, if the relationship between molecular orientation and flow were better understood, spinnerets could be designed to optimize molecular orientation of the as-spun fiber. Improvements such as these, combined with the more efficient graphitization ovens, offer promise for reducing the price of high-thermal-conductivity pitch-based carbon fibers.

As with PAN-based carbon fibers, while incremental gains in properties might be expected, the major effort for pitch-based carbon fibers will most likely be toward price reduction. Success could finally create the high-volume market needed to make pitch-based carbon fibers a commodity product. To create this market, investment is needed to develop a better understanding of how to design with pitch-based composites and of how to process and control the composite microstructure to get the best thermal conductivities.

*Opportunities*

- Investment in the evaluation and installation of new continuous process monitoring techniques (such as online Raman spectroscopy) could be valuable in the near term by improving the purity of the fiber precursor, enhancing the uniformity of fiber structure, and reducing property variability for both PAN- and pitch-based carbon fibers.
- Initiate fundamental studies for both PAN- and pitch-based carbon fibers to develop molecular orientation during flow, solidification, and heat treatment.
- Provide funding for new analytical methods such as MALDI that could lead to improved precursors for pitch-based carbon fibers and carbon-carbon matrices.
- Invest in studies with revolutionary approaches to aid design and development pitch-based composites for thermal management applications.

### *Organic Fiber Improvements*

In Chapter 2, the committee expresses an opinion that incremental improvement in tensile properties (especially strength) is still possible, and even likely, for those fibers that are commercially available today. The new developments are likely to be aimed at increased toughness and energy

absorption, since this is the area in which these materials offer an advantage over carbon fibers. The development may be a result of research aimed at specific fiber properties and at optimization of ways in which the fibers are incorporated into the final structures.

All materials commercially available at this point are a result of many years of product and process development as well as many years of manufacturing experience. All of them operate in a very competitive environment. Thus, one would not expect downward changes in the prices of these materials. Nevertheless, opportunities do exist to lower the cost of utilizing them. These can be realized through better designs of the systems in which they are included. This is an area in which DoD-sponsored research activities would be highly cost-effective. The details are discussed in later sections.

Additional efforts toward developing engineering standards for the use of organic fiber composites would also be very beneficial. Such standards are necessitated by the extreme anisotropy of properties of these materials. For example, the modulus of these fibers in the direction parallel to the fiber axis is two orders of magnitude greater than the modulus in the direction perpendicular to the fiber axis. The same is true of strength. Relatively low lateral properties significantly alter the mechanism of failure compared to traditional materials. Even when advanced fibers are exposed to tensile stresses, they fail in shear. The same phenomenon is responsible for their relatively low compressive properties. The increase in lateral interaction observed in aramids compared to polyethylene improves the compressive properties of aramid composites to a noticeable degree.

There are several examples in which a systems design approach has helped to circumvent deficiencies in component materials. For example, tires can be designed in such a way that the reinforcing fiber is never put into compression. Use of release technology (to decrease adhesion between the fiber and the resin) to minimize impact of low lateral properties and prevent longitudinal failure is another possibility. These are only two examples of many options that are possible. Research in both of these areas would improve the chances of meeting DoD needs with existing materials for which pricing is defined by competitive forces in the civilian marketplace.

### *Improved Compression Performance of Organic-Based Fibers*

The exception to the trend of incremental improvements is the newest fiber M5®, which is in late development stages. Although the fiber is expected to be available on a commercial scale in 4 to 5 years, it is likely to reach a large commercial scale a bit later. It has been shown that fibers produced from this material exhibit bidirectional intermolecular hydrogen bonding. This hydrogen bonding should greatly increase the internal shear modulus of the fibers and may result in improvements in mechanical properties in tension and compression. As these properties are realized, a combination of ballistic properties and the ability to function as a structural component has the potential to revolutionize armor development in terms of weight reduction. DoD should fund opportunities to evaluate the properties and applications of M5 once adequate qualified capacity is established.

### *Matrices and Interphase*

Although the fibers are of great interest, the matrix and interphase are also important constituents of the composite system. In general, advanced resin formulations are needed that feature low cost, room-temperature cure, low viscosity, improved toughness, dimensional stability, and long-term environmental durability. Further, it is particularly important for the resins to be compatible with lower-cost manufacturing methods such as VARTM and e-beam curing.

VARTM is being considered by all services as an affordable process. The Army requires VARTM resins that can be infused at room temperature, be cured at low temperature, and provide improved multi-hit ballistic and structural performance in ground vehicle hull structures. In parallel, studies on sizings for tailored ballistic and structural properties for the new resins are needed.

Navy ship applications require resins that can be processed through VARTM with improved fire, smoke, and toxicity performance. The new resins should be developed in parallel with new fire-resistant core materials, with an emphasis on adhesion since sandwich construction is a common design feature. There are some significant opportunities for concurrent investment in refining current chemistries (phenolics) and developing new ones (e.g., low-viscosity preceramic polymers). In addition, the use of carbon fiber with vinyl ester VARTM resins for ship structure requires additional study of sizings to

promote adhesion and durability of the composite. The new class of low-viscosity cyclic thermoplastics that polymerize after infusion offers the potential for improved toughness in VARTM-fabricated structures.

Electron-beam (e-beam) curing is a nonthermal process that uses high-energy electrons and/or X-rays to initiate polymerization and crosslinking reactions at controlled rates at room temperature. The primary challenges facing the current state-of-the-art e-beam resins are the lack of toughness, hot-wet operating temperature limits, and consolidation rheology. Long-term durability of composites may also require optimization of the fiber-matrix interface that forms during e-beam processing.

## *Composites*

As stated earlier, gains in fiber performance over the next 5 to 10 years are likely to be incremental rather than revolutionary (with the possible exception of M5). The same can be said for matrix resins and for composites made using these matrices and fibers. Although there are longer-term opportunities for greater performance leaps (discussed later), the next decade will generally be characterized by continuous improvement of existing composite systems. Types of improvements might include incremental increases in strength and stiffness, better fiber-matrix interface strength and/or durability, enhanced damage resistance and damage tolerance properties, and processing advancements.

One exception is the emerging area of multifunctional composite materials where composites, as man-made materials, are the ideal host to incorporate a full spectrum of functionality for personnel protection (ballistic and extremity protection, biological and chemical protection) and structural applications (ballistic and blast protection) at minimum weight. Multifunctional composites can also provide the foundation for the integration of signature management, communication systems, power grids, and sensor arrays.

It is recognized that the development of multifunctional composites for armored vehicles, topside ship structures, and unmanned robotic and aerial vehicles will require continuous DoD investment. In the near term, current fibers, resins, and processes can be used to create first-generation multifunctional composites. Ideally, each layer in the composite will serve multiple functions. The near-term challenges are twofold: (1) design methods to predict the optimum grading of layer functionality to achieve performance requirements; (2) advances in processing science to enable integration of functionality and manufacturing for scale-up into affordable components and structures for test and validation. The creation of such composites will require prudent investment as well as vision on the part of DoD program managers.

### *Multifunctional Composite Armor*

The U.S. Army is undergoing a transformation to a more agile, lighter, and more lethal force. Current acquisition focuses on the Medium Brigade, which will consist of C-130-transportable wheeled vehicles using existing armor technologies (principally metals and composite spall liners). In the mid-term, the Future Combat System (FCS) will be fielded and will become a "system of systems" integrating land, air, and soldier missions. The plans for block upgrades of technology offer significant opportunities for the insertion of new materials and affordable processes. Current state-of-the art armor used in the Composite Armored Vehicle Advanced Technology Vehicle combines ceramics and composites to provide structure and ballistic protection at areal densities of 25 pounds per square foot. FCS vehicles will require significant reductions (20 to 50 percent) in areal density for various platforms and a level of multifunctionality not achieved in previous systems.

In addition, crew protection kits for tactical vehicles are needed to increase protection levels. Steel kits currently being deployed in Iraq are too heavy and exceed the gross vehicle weight, thus leading to increased maintenance, repair, and replacement. Multifunctional ultralightweight armor that provides structure and improved protection against projectiles and improvised explosive devices is needed in the near term.

Significant DoD investment is necessary to enable multifunctional composite armor incorporating lower-density fibers such as carbon and organics (e.g., Kevlar, Spectra, and PBO) that provide adequate structure with improved ballistic performance to achieve these objectives. The M5 fiber offers a potential to combine improved compression properties with excellent ballistic performance that should be evaluated for structural armor applications. In addition, three-dimensional preforms that can be hybridized with multiple fibers offer great promise for structural armor and blast protection. Significant

investment in materials development concurrent with the design and manufacturing of these new classes of multifunctional armors and structures is needed to ensure that affordable technologies are ready for insertion into current and future tactical vehicles and other FCS systems, as well as Navy hull and ship topside structures.

In aircraft structures, it is widely recognized that material costs are a small percentage of total acquisition cost. Although composites, by their nature, lend themselves to single operation co-curing of large and complex structures, assembly costs still represent a significant contribution to overall cost. When assembly of subcomponents is necessary, good fit (without the need for rework or additional operations) is essential. Improved dimensional tolerance via materials and processing would provide a significant cost reduction in assembly and thus the use of composites. The cost of refit can be up to 30 percent of the total composite part cost.

Recent activities promise an excellent start in understanding how to improve dimensional tolerance and determining which parameters are critical in controlling dimensional tolerance.[3] These studies determined that fiber variability from lot to lot (density, filament diameter, filaments per tow, etc.) plays a significant role in fit and assembly issues and identified prepreg processing steps that could alleviate some problems. Further studies into the root causes of poor dimensional repeatability would help to address this concern and identify which parameters are major contributors.

A current trend across the industry is the assessment of VARTM to replace more costly processes in DoD and commercial applications. VARTM has been the process of choice for fabrication of large-scale ship prototype structures. The VARTM process is being critically evaluated for aerospace applications as an alternative to RTM. VARTM is also the leading candidate to manufacture the multifunctional composite armor previously discussed.

VARTM is widely accepted as an affordable process to fabricate prototypes. VARTM is a low-pressure process that offers reduced tooling costs. Fiber volume fractions and associated properties are lower than for higher-pressure processes, so parts processed using VARTM might have to be heavier to meet the same performance requirements as parts fabricated by a traditional process. VARTM uses one-sided tooling, and strict control of geometry is not yet possible and may add to assembly costs. The process is largely a manual process lacking quality control and automation.

Due to the widespread interest in the VARTM process, it is recommended that DoD initiate a program with university-industry-government participation. Virtual manufacturing and simulation should play an important role in accelerated insertion of materials and processes into DoD systems. Advancements in intelligent processing will allow for risk and cost reduction, but advances in three-dimensional flow simulation in porous media are also required, as well as models to predict input properties such as the permeability tensor as a function of fiber architecture, compaction, and distortion. A key element of this effort will be the transfer of technologies developed in universities into the industrial base. This will require education and training as well as software and hardware deployment. Industry will conduct manufacturing trials and quantify the cost and performance trade-offs. Research in automation using simulation, sensing, and control systems should be pursued to advance this process from prototype to a production-ready process.

## OPPORTUNITIES TO IMPROVE PROGRAMMATIC EFFICIENCY

### *Improved Building Block Certification Approach*

Mechanical testing of full-scale structures or large components can be extremely costly in terms of both program resources and program risk. Large-scale testing facilities require expensive, specialized equipment, and the test article itself is costly to fabricate and instrument. In addition, a single test of a large component may take weeks or even months to set up and complete. Thus, savings can be gained by reducing the quantity of these types of tests. From the standpoint of risk, a program may incur a severe setback in terms of redesign, material substitutions, or process changes if large-scale tests do not produce the required or expected results.

[3] Prime contracts referenced include Precision Assembly for Composite Structures, F33615-96-2-50051 (Boeing), Processing for Dimensional Control, F33615-97-C-5006 (Boeing), and Reduced Dimensional Variation in OMC Lay-Ups, F33615-97-C-5007 (GE Aircraft Engines).

Clearly, for complex composite products, the large-scale or full-scale test should serve as the final check on the entire process of product and process development, and there should be little risk of surprises at this stage. To both reduce the number of large-scale tests and have confidence that a product will meet design requirements, a structured approach to the qualification and certification process is needed. Such an approach has been used, particularly in the aircraft industry, and has become known as the "building block" approach because it comprises a number of stages (or blocks). Each block consists of testing and analysis that increase in complexity with each successive block and builds on knowledge gained in previous blocks.

Although the concept of the building block approach is widely acknowledged in the composites industry, it is applied with varying degrees of rigor, and details are far from universal.[4] This lack of standardization has hindered exploitation of the full potential of this approach. Ideally, a building block program is aimed at obtaining information at the lowest possible level of complexity and using analysis rather than testing as much as possible to minimize cost. Cost-efficiency is achieved by testing greater numbers of less expensive small specimens and fewer of the more expensive components and full-scale articles. At the same time, the process should provide a means of assessing technology risks early in a program to reduce the probability of unanticipated results in the final stages of certification. Although there have been some attempts at detailing the specifics of the building block approach and standardizing the methodology,[5] more work needs to be done in this area.

Based on the above, DoD funding could be directed in several ways to promote the standardization and efficiency of the building block process. One area that needs study is statistical continuity throughout the process. Currently, there are rigorous statistical methods for selecting the numbers of specimens tested at the lowest building block level (coupon testing to obtain material property basis values). However, this statistical precision has not been carried forward to the element, subcomponent, and component levels. Quantifying the statistical significance of numbers of test articles at the higher levels could help to reduce the amount of these more expensive tests. A related subject for research is the development of a well-defined methodology for maximizing the use of data obtained at lower building block levels in order to minimize the quantity of higher-level testing. In addition to specific research projects, continued and expanded funding of the MIL-HDBK-17 coordination activity would serve to maintain an industry-wide forum for review of building block methodology.

Part of the limitation in developing the correlation from the coupon level to the subcomponent and component level is our poor understanding of how the stochastics of the failure process in a small coupon translate into stochastics of failure at the component level. To gain this understanding, a rather rigorous and large program of experimentation and modeling is required, and DoD funding in this area would be an excellent investment.

### *Improved Mechanical Test Selectivity*

When a composite material is qualified to a specification and characterized to provide basic lamina and laminate mechanical properties, testing is performed with a variety of loading types at several environmental conditions. Typically various tension, compression, and shear tests are conducted in four or five different dry and wet environments. Although the current testing may provide very complete characterization, it is not clear that all of these tests are necessary. Composite material procurement specifications represent one area in which unneeded testing may be imposed. Procurement specifications frequently state a required value for nearly every mechanical property in multiple environments. In its simplest form, a procurement specification has only two functions: (1) to describe the material adequately so that there is no doubt about what is being purchased and (2) to provide a means of assuring that quantities of material purchased over time are the same (within a given tolerance) as the material originally qualified. Since certain properties and conditions tend to be more reliable indicators of material variability than others, the committee believes that specifications could be simplified to include fewer tests and conditions if an optimum set of tests were defined. For example, test frequency could be reduced once qualified materials are in production.

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[4] MIL-HDBK-17, 1998.

[5] See, for example, R.S. Whitehead, H.P. Kan, R. Cordero, and E.S. Saether. 1987. Certification testing methodology for composite structures. NADC-87042-60. Warminster, Pa.: Naval Air Development Center.

This same concept applies to the testing performed to characterize the generic lamina and laminate properties in the early stages of a building block certification program. Since particular properties and conditions tend to become the important design drivers, there is little need to extensively test noncritical loadings and environments.

Although small-specimen coupon testing is not as costly as higher-level building block tests, there may be opportunities for significant savings if the quantity of such testing could be reduced. To achieve this, DoD-funded research could be directed toward determining which types of tests and environments are insignificant as design drivers for given classes of applications. The result of such research would be recommendations for elimination of certain tests for particular applications. Such recommendations would have to be based again on a large-scale study using both experiments and modeling. In addition, DoD-funded research could be focused on standardization of procurement specifications. While this goal has been attempted by a number of organizations over the years, there has been no nationally funded program to sustain the effort and bring about its implementation.

### *Use of Historical Test Data to Support Development of Analytical Methods*

As stated earlier, the use of analysis is generally less expensive than conducting mechanical tests. Although some level of testing will always be necessary to verify analytical predictions, advances in analysis methods are continually needed to drive the testing requirement to a minimum. However, to develop and validate new and robust analytical methods, a body of test data is needed that covers various types of materials, laminate configurations, loading conditions, and environments. Although much testing has been conducted for various DoD and Federal Aviation Administration (FAA) programs during recent years, these data are not available in a readily usable form. If these data could be compiled, categorized, and documented, the developers of analytical methods could, in some cases, draw on these data rather than conducting new tests. Areas in which current analysis methods are weak, and where historical data would be beneficial, include compression after impact (both solid laminate and sandwich structure), mechanically fastened joints, delamination growth, and fatigue. To achieve this, DoD might consider funding an effort to compile coupon, element, and subcomponent test data from recent certification programs and make it publicly available in a standard format. The payoff would be the acceleration of analysis method development to further reduce the need for numerous larger-scale tests.

## LONG-TERM (MORE THAN 10 YEARS) PERFORMANCE GAINS

In the following sections, the committee identifies strategic research areas in fibers, matrices, interfaces, and composites that may require a decade or more to bear fruit. Although these research thrusts carry a higher risk of failure than the nearer-term opportunities identified above, they would, if they are successful, produce dramatic performance gains for composite structures.

### *Nanoscale Fibers*

Using current technology and precursors, only incremental improvements in fiber properties will be achieved. Fibers with controlled nanostructure have the potential, however, to achieve step changes in properties. In addition, nanoscale fibers may have niche applications in sensors or other low-volume applications.

Nanoscale fibers are those with a diameter of less than 100 nanometers. Their surface area is more than 100-fold that of conventional fibers. The two major classifications of nanofibers are those processed from polymers, and those inorganic fibers that are grown (including carbon nanotubes).

Polymer nanoscale fibers can be woven into unique fabrics with high surface area and small pore size. This makes nanofiber textiles excellent candidates for barrier materials to protect against chemical and biological weapons as well as environmental threats such as wind and rain.[6] This large amount of surface area also provides a convenient platform to place arrays of sensors. Conductive nanofibers

[6] K. Graham, H. Schreuder-Gibson, and M. Gogins. 2003. Incorporation of electrospun nanofibers into functional structures. Presented at International Nonwovens Technical Conference 2003, sponsored by the Association of the Nonwoven Fabrics Industry (INDA) and the Technical Association of the Pulp and Paper Industry (TAPPI), Baltimore, Md., September 15-18.

woven throughout a soldier's uniform could serve as a grid to bring power to—and to convey information from—the host of nanoscale sensors that will be part of the future soldier system.

Polymer nanofibers also have potential use in ballistic protection applications. On average, the defect size in a nanometer-diameter fiber is smaller than the average defect size in a conventional fiber. Therefore the critical stress required to fracture a nanofiber could be much greater than that of a conventional fiber. The high surface area of nanofiber textiles will also greatly help to transfer the load of an impact to the surrounding fabric, promoting energy dissipation over a larger area. By producing nanofiber textiles from high-performance polymers such as Kevlar KM2 and PBO, whose surface can be functionalized to perform multiple duties, there is the potential to make a single, breathable, multifunctional fabric that will defend the soldier from the full spectrum of threats. One limitation of this application is that production rates for nanofibers are inherently slow; therefore, nanofibers might be better used in small-scale niche applications or woven into traditional fabrics, thus providing the sensing and power functionality only.

Multifunctional armor is also an essential component of a future soldier's system and will rely heavily on organic fibers that can be converted into protective clothing. The Interceptor system combines a Kevlar vest with ceramic armor inserts. The Land Warrior soldier system is the first fully integrated system that provides protection from the full spectrum of threats (ballistic, chemical, biological, environmental), but it is moderately heavy (92 pounds). The Objective Force Warrior (OFW) is the Army's current effort in soldier system design led by a lead system integrator. The goal of OFW is to design with the goal of taking the advances achieved in the Land Warrior program to the next level of development by reducing the soldier's overall load to 35 percent of his body weight and providing greater capability in signature management, threat protection, information gathering, and troop coordination.

In support of the OFW program, the DoD funds a wide variety of academic and industrial research programs[7] that address power generation, advanced sensor development, robotics, and microclimate control. Success in each of these areas is being driven by revolutionary advances in microelectronics, biochemistry, and materials processing on increasingly smaller length scales, approaching the nanoscale regime. This added functionality is likely to be integrated into the soldier's clothing fabricated with organic fibers in the submicron range. The most recent developments indicate that commercial sources of such materials will become available in the near future. Significant investment of DoD resources into nanofibers, materials, and devices is warranted to meet the long-term objectives for soldier protection.

*Carbon Nanotubes*

Carbon nanotubes are quasi-one-dimensional, nearly single-crystalline (axially), hollow, graphitic carbon structures. Two varieties of carbon nanotubes exist: single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs). The first nanotubes observed were multiwalled nanotubes. MWNTs consist of two or more concentric cylindrical shells of graphene sheets arranged coaxially around a central hollow core with interlayer separation as in graphite (0.34 nm).[8] In contrast, single-shell or single-walled nanotubes[9,10] are made of single graphene (one layer of graphite) cylinders and have a very narrow size distribution (1-2 nm). Often many (tens of) single-shell nanotubes pack into larger ropes. Both types of nanotubes have the physical characteristics of solids and are microcrystals, although their diameters are close to molecular dimensions. In nanotubes, the hexagonal symmetry of the carbon atoms in planar graphene sheets is distorted because the lattice is curved and must match along the edges (with dangling bonds) to make perfect cylinders. This leads to a helical arrangement of carbon atoms in the nanotube shells. Depending on the helicity and dimensions of the tubes, the electronic structure changes considerably.[11,12] Hence, although graphite is a semimetal, carbon nanotubes can be either metallic or

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7 Examples include Multidisciplinary University Research Initiatives (MURIs) through the Army Research Office (ARO), Collaborative Technology Alliances (CTAs) through the Army Research Laboratory (ARL), and contracts through the Defense Advanced Research Projects Agency (DARPA).

8 P.M. Ajayan and T.W. Ebbesen. 1997. Nanometre-size tubes of carbon. Reports on Progress in Physics 60:1025.

9 S. Iijima and T. Ichihashi. 1993. Single-shell carbon nanotubes of 1-nm diameter. Nature 363:605.

10 D.S. Bethune, C.H. Kiang, M.S. de Vires, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers. 1993. Cobalt-catalyzed growth of carbon nanotubes with single-atomic-layer walls. Nature 363:605.

11 J.W. Mintmire, B. Dunlap, and C.T. Carter. 1992. Are fullerene tubules metallic? Phys. Rev. Lett. 68:631.

semiconducting. Nanotubes are closed by fullerene-like end caps that contain topological defects (pentagons in the hexagonal lattice). The electronic character of the ends of these tubes differs from that of the cylindrical parts of the tubes and is more metallic due to the presence of defects in these regions.[13]

Both SWNTs and MWNTs are currently available in micron lengths, and longer lengths have been made in the laboratory. The topology of nanotubes indicates extremely high thermal and electrical conductivity in the axial direction, and the measured longitudinal elastic modulus is in the terapascal range—higher than that of any known material. The combination of high aspect ratio, small size, strength, stiffness, low density, and high conductivity makes nanotubes extremely intriguing candidates as fillers in polymer composites or in polymer precursors for graphite or aramid fibers. Multiwalled hollow nanofibers (with about eight layers of nanotubes) are also being made in a configuration much like steel wool using a catalytic chemical vapor deposition technique.[14]

Several small companies are currently producing SWNT in quantities of kilograms per day.[15] Current purified material costs around $500 per gram. These prices have the potential to decrease dramatically as volume increases and other continuous processing methods are developed. A complication here is that the perfection—and thus the properties of the nanotubes—is strongly affected by such processing methods as pulsed laser deposition, electric-arc discharge, or high-pressure carbon monoxide conversion.

The high price, combined with dispersion issues and size distribution issues, makes the use of nanotubes as reinforcing fibers on their own a very long term project. There are, however, other opportunities for nanotubes that take advantage of their high electrical conductivity and large surface area. For example, the addition of less than 1 weight percent of nanotubes to polymers can increase their conductivity by eight orders of magnitude and can increase the glass transition temperature by tens of degrees. This can justify the use of nanotubes to modify matrix materials. In addition, nanotubes could be used in other combinations to make unique fibers. There have been reports of nanotube composite nanofibers with a combination of strength and modulus that cannot be achieved with other fibers.[16] Continued investment in long-term research on the use of nanotubes to modify matrix behavior can only lead to more of these innovations.

*Nanostructured Micron-Scale Fibers*

Nanoscale fillers offer an opportunity to control the nanostructure of fibers. Work is already going on in pitch-based fibers[17] and PAN precursors.[18,19] Current pitch precursors lead to extended graphitic structures that make the fibers flaw sensitive. By adding small quantities of nanotubes to mesophase precursors, the balance of properties might change.[20] One could expect the nanotubes to nucleate domains within the mesophase. Smaller domains might be expected to decrease the flaw sensitivity of the fiber and increase its strength. Initial results demonstrate that the domain size is indeed reduced. However, the nanotubes were not dispersed uniformly in the mesophase and the expected improvement in fiber strength was not observed. While this initial study provides no conclusive proof that combining nanotubes and mesophase can improve the balance of properties for pitch-based fibers, it offers some

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[15] For example, by Carbolex in Lexington, Ky., and Carbon Nanotechnologies, Inc., in Houston, Tex.

[16] A.B. Dalton, S. Collins, E. Munoz, J.M. Razal, V.H. Ebron, J.P. Ferraris, J.N. Coleman, B.G. Kim, and R.H. Baughman. 2003. Super-tough carbon-nanotube fibres. Nature 423(6941):703.

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[18] T.V. Sreekumar, T. Liu, B.G. Min, H. Guo, S. Kumar, R.H. Hauge, and R.E. Smalley. 2004. Polyacrylonitrile single-walled carbon nanotube composite fibers. Advanced Materials 16(1):58-61.

[19] F. Ko, Y. Gogotsi, A. Ali, N. Naguib, H. Ye, G. Yang, C. Li, and P. Willis. 2003. Electrospinning of continuous carbon nanotube-filled nanofiber yarns. Adv. Mat. 15:1161-1163.

[20] T. Cho, Y.S. Lee, R. Rao, A.M. Rao, D.D. Edie, and A.A. Ogale. 2003. Structure of carbon fiber obtained from nanotube-reinforced mesophase pitch. Carbon 41(7):1419-1424.

hope that this may be possible. If nothing else, it proves that the addition of nanotubes can reduce the domain structure of mesophase pitch. This alone could allow better control of the matrix structure in carbon-carbon composites formed from mesophase matrices. In PAN precursors, the addition of SWNTs leads to improved thermal stability and higher modulus of the precursor fiber.[21] The carbonized fiber has higher modulus than pure PAN-based carbon fibers and the same strength.

There is evidence that the approach of incorporating single-walled nanotubes into precursors is highly effective and worthy of further investigation in order to obtain a step change in fiber properties. Significant investment in processing and structure control is necessary before such fibers could be commercialized. Attention to potential environmental, safety, and health concerns is also warranted in light of past experience with other small fibers.

## *Advances in Fiber Processing*

Because of their characteristic fibrillar structure, polymeric precursor fibers are preferable for producing high-strength carbon fibers. Although prices for carbon fiber from SAF- and textile-based precursors prices have dropped to an all-time low, current PAN-based processes are unlikely to allow further cost reduction. Alternative, potentially low-cost routes for producing this class of carbon fibers should be explored. These should include more efficient processes for producing PAN, rather than the current wet-spinning technique, and exploring alternate methods that can decrease stabilization times and/or reduce the amount of oxygen added during stabilization and, thus, increase overall process conversion. Also, potentially low-cost precursor polymers with higher carbon contents should be evaluated.

### *Melt Spinning of Mesophase Pitch Fibers*

High-thermal-conductivity fibers are melt-spun from a liquid crystalline mesophase pitch precursor. The current domestic process for producing mesophase pitch involves thermal treatment of an isotropic pitch precursor. The molecular weight distribution of the resulting product is relatively broad. Although the process is relatively simple, research has shown that more uniform mesophases develop higher degrees of molecular orientation during fiber formation and graphitize more readily during final heat treatment. The development of cost-effective new processes for producing mesophase precursors and techniques controlling the structure of the mesophase during fiber formation could reduce final heat treatment temperatures by as much as 600°C. This alone would reduce production costs by a factor of 10, making high-thermal-conductivity carbon fibers attractive for high-volume applications such as consumer electronics and automotive brakes.

### *Nanofiber Processing*

A number of processing methods can be used to obtain polymer nanofibers. These include electrospinning, various types of melt blowing, controlled phase separation of polymer blends during melt spinning, and self-assembly of biomolecules into fibrous structures. All of these processing techniques are in relatively early stages of development, and there is much work yet to be done.

### *Modeling and Real-time Characterization of Fiber Spinning Processes*

Thanks to the rapid advances in digital technology that have occurred over the last decade, it has become possible to obtain real-time spectroscopic (infrared, X-ray scattering, Raman) and imaging data for a variety of polymer processing techniques including fiber spinning. Such data provide insight into the influence of processing variables on the molecular ordering and phase transitions that occur during fiber spinning. This molecular ordering (or lack thereof) ultimately determines the mechanical properties of high-performance fibers. More accurate theoretical models can be developed based on this information, which can then be used to optimize processing conditions in order to produce the highest-quality fibers. These real-time characterization techniques provide a feedback mechanism on the molecular scale that

[21] T.V. Sreekumar, T. Liu, B.G. Min, H. Guo, S. Kumar, R.H. Hauge, and R.E. Smalley. 2004. Polyacrylonitrile single-walled carbon nanotube composite fibers. Advanced Materials 16(1):58-61.

until recently was either not possible or prohibitively expensive. Such feedback will only increase in importance as the individual fibers themselves become composites through the addition of nanoparticulates such as layered clay silicates and carbon nanotubes. Wise investment in this type of basic research will lead to a reduction in the time required to develop new fibers and will also accelerate the optimization of current commercially available fibers.

### *Opportunities*

- Investment in more efficient processes for producing PAN precursor fibers (such as melt spinning rather than the current wet-spinning technique) and alternate methods that can decrease stabilization times and/or reduce the amount of oxygen added during stabilization—and thus increase overall process conversion—should be considered. Also, potentially low-cost precursor polymers with higher carbon contents should be evaluated. Investment in these areas could yield long-term cost and performance benefits for DoD systems.
- Investment in programs developing new nanostructured (micron-scale fibers with nanoscale structure) and nanoscale-diameter fibers is critical to fibers exhibiting a step change in properties.
- Investment should be made in fundamental studies that couple online monitoring of the development of molecular orientation during flow, solidification, and heat treatment to the verification of fundamental process and product models that incorporate molecular detail. This type of basic research, now possible because of growing computer power and advances in computational materials science, could greatly reduce the time required to develop new classes of fibers and lead to improved properties in current commercially available fibers.
- Improved techniques for measuring the composition of pitch and more cost-effective new processes for producing mesophase precursors should be developed, and techniques for controlling the structure of the mesophase should be funded.

### *Advances in Matrixes*

Controlled architecture of matrix materials is possible using bio-inspiration and self-assembly techniques. While this is an important area for future investment, there has already been significant investment in this area.

One opportunity for improving resins is the addition of nanoscale filler. This would lead to a hierarchical composite with nanocomposite resin embedding traditional fiber structures. The main advantage of nanofillers is that they can provide multifunctionality to the resin (e.g., improved toughness and conductivity or improved toughness and UV absorption). The challenges include increased resin viscosity and the possibility of filtering out nanofillers leading to inhomogeneous distribution. Nevertheless, there are hints of success in this area. A recent paper showed that the addition of multiwalled carbon nanotubes to epoxy for use as an adhesive to join two graphite-epoxy composites resulted in about a 40 percent improvement in the average shear strength of the lap shear joint. The failure occurred inside the graphite fiber composite instead of in the adhesive. This success was observed at a loading of 5 weight percent MWNT.[22] Nitrogen-doped nanotubes have been found to increase the glass transition temperature of epoxy by as much as 25°F. Increases in electrical conductivity of as much as eight orders of magnitude at 1 weight percent of filler have been observed.[23,24]

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[22] K.-T. Hsiao, J. Alms, and S.G. Advani. 2003. Use of epoxy/multiwalled carbon nanotubes as adhesives to joint graphite fiber reinforced polymer composites. Nanotechnology 14:791-793.

[23] A. Eitan, L.S. Schadler, J. Hansen, P.M. Ajayan, R.W. Siegel, R. Andrews, and M. Terrones. 2002. Processing and thermal characterization of nitrogen doped MWNT/epoxy composites. Proceedings of the 10th US-Japan Conference on Composite Materials, Stanford University, Stanford, Calif., September 16-18.

[24] J. Coleman, A. Dalton, S. Curran, A. Rubio, A. Davey, A. Drury, B. McCarthy, B. Lahr, P. Ajayan, S. Roth, R. Barklie, and W. Blau. 2000. Phase separation of carbon nanotubes and turbostratic graphite using a functional organic polymer. Adv. Mater. 12:213.

Another fruitful area of research is the use of self-healing polymers as matrices in composites. In these systems, microcracking has been identified as one of the first damage modes, and self-healing polymers will be effective in increasing the long-term durability and life of composites.[25-27]

### *Interface and Interphases*

A designed interface is crucial to controlling composite properties. Several areas are worthy of investment here. First, interdisciplinary studies are needed in which molecular-scale modeling is coupled with new chemistry to create sizings that have controlled coupling between matrix and fiber, and to create an interphase region that contributes to optimized properties. Recent studies have shown that incorporating nanoparticles into fiber sizings offers improvements of strength and energy absorption for structural armor applications and represents a new mechanism for tailoring properties. This interdisciplinary approach is critical to success. Second, combined studies are needed involving the chemical industry, the fiber industry, and new chemistry, to test the effect of sizings at the bulk scale.

### *Composites*

In 10 to 20 years, next-generation composites are likely to include the maturation of current materials and processes as well as the introduction of new fibers of increasingly small diameters, nanoreinforced resins and interphases that will provide levels of multifunctionality that cannot be achieved with current materials. In both cases, improvements in design methodology are needed.

Current materials can be optimized to extract their full potential as discussed below. However, next-generation materials will require new multiscale modeling methods to bridge the molecular interactions between constituents and the overall performance of the composite systems. It is also recognized that the processing science of multifunctional composites materials incorporating nanoscale constituents and devices must be developed. Investment of funding in these areas now is necessary to develop the design and processing methods of the future.

### *Developing a Better Design Methodology*

One of the clearest messages that came from the committee's study is that designers are not taking full advantage of current composite systems. Available materials systems are not optimized, and the properties of composites are not understood well enough to design properly. In addition, because of the variability in composite properties, an extremely conservative design is used that typically adds weight and cost. Finally, the part design is often completed without the material system in mind. In order to develop a better design methodology, the following will be necessary:

- Understand the role of each constituent in controlling properties, particular damage development and failure. This requires developing an experimental database from carefully controlled systems in which only the interface, or only the fiber, or only the matrix is changed, to determine the role of each. In addition, these data must be obtained for specific processing methods.
- Incorporate statistical mechanics into property predictions at the micromechanical level. This should include constitutive laws that model polymer deformation and failure appropriately.
- Develop new design tools that incorporate information from the database and the new models.

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[25] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, and S. Viswanathan. 2001. Autonomic healing of polymer composites. Nature 409:794-797.

[26] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, and S. Viswanathan. 2002. Autonomic healing of polymer composites. Nature 415:817.

[27] E.N. Brown, S.R. White, and N.R. Sottos. 2004. Microcapsule induced toughening in a self-healing polymer composite. Journal of Materials Science 39:1703-1710.

- Understand the residual stress gradients and defects that develop under specific manufacturing processes.

The first opportunity requires some significant, focused funding that involves the fiber manufacturers, resin manufacturers, composite processors, and either academia or a large neutral testing facility. A carefully designed set of experiments is needed that would alter fiber properties, fiber strength distributions, interface properties (using some of the new interfaces developed in academia), and matrix properties and then characterize the resulting interface behavior, as well as the macroscopic tensile, compressive, fatigue, creep, and toughness behavior as a function of each variable. Although a few studies have attempted a portion of this, no large-scale study has been conducted.

The second opportunity is in the area of modeling of properties. Continuum models must be linked to micromechanical models and perhaps even molecular-level models. The fiber and interphase property variations must be included and the nonlinear behavior of the matrix must not be ignored. The modeling must consider the thermal and stress gradients that develop for a given processing method, as well as the thickness and curvature of the final part. Realistic modeling of the processing defects that occur must be included.

Finally, the stochastics of the failure process and how it translates from small samples to the component level must be considered. This is a difficult task, but a great deal of progress has been made in this area recently.[28]

### *Interdisciplinary and Interinstitutional Development*

A common theme in the committee's discussions was the appropriate role of academic research in the development of the fiber and composites industry. There has often been a disconnect between academic and industrial research efforts in the composites area. For example, the academic community has studied interfaces in great detail, but often the technology developed—and the fundamentals learned—are not used by industry, either because of poor transfer of technology, poor use of the literature by companies, or the inability to scale the interfaces developed. Even when industry is aware of developments in academia, the time and resources required to redevelop the expertise in the industry are often considered too high. On the other hand, most academic facilities cannot produce fibers, interfaces, matrices, and composites and thus rely on industrial materials. Although the field is highly proprietary (making it difficult for academics to get information to study their materials properly or for industry to share), there are some precompetitive issues that would best be addressed by a collaborative, interdisciplinary or interinstitutional research program facilitated by government.

The committee did not specifically explore the form that such interinstitutional collaborations might take: it merely notes that the current paradigm of academia studying model materials—or materials that it is not allowed to completely characterize—leads to less than ideal science.

[28] A.M. Sastry, C.W. Wang, and L. Berhan. 2001. Deformation and failure in stochastic fibrous networks: Scale, dimension and application. Key Engineering Materials, Trans Tech Publications 200:229-250.

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# Conclusions and Recommendations

When high-performance carbon fibers were first developed in the 1960s, their high cost (as much as $400 to $500 per pound) limited their applications to high-value military aerospace and space systems. The results of early military composite development programs may be seen today in systems fielded by each of the military services. For example, more than 350 parts of the F-22 Raptor, accounting for 25 percent of its structural weight, are carbon-epoxy composites.[1] Further, the developmental Joint Strike Fighter will be between 25 and 30 percent composite by weight. The Army now uses carbon-thermoplastic composites in high-volume production of sabots for the M829A3 munition.

## FINDINGS AND CONCLUSIONS

### *Fiber Supply*

The 2004 worldwide capacity of carbon fibers (SAF based and textile precursor based) was expected to be more than 70 million pounds. Consumption was expected to be more than 40 million pounds and increasing. In this changing market, it appears that each carbon fiber supplier has targeted specific market segments and is building facilities and directing product portfolios to support its chosen strategies. Although some producers have indicated that the high cost of adding new facilities is a barrier to increasing capacity, DuPont, Honeywell, Dyneema, Toho, and Toray are all adding capacity in the United States. This added capacity will help to meet the anticipated shortage of carbon fiber produced with SAF precursor and meet the demand for organic fiber for military and homeland security applications.

Significant investment has been made over the past 4 to 5 years in capacity for *p*-aramid and PE fibers. Some of this capacity has been developed for military products, but most is targeted toward nonmilitary applications. Current expansion is targeted to meet the military needs for soldier protection and homeland security. An important aspect of this continuing investment is an M5 pilot plant start-up planned for 2005. This new M5 capacity will enable ballistic and structural performance evaluation to be conducted on full-scale components.

### *Fiber Demand*

As the fiber industry matured during the 1980s and costs began to decrease, a variety of commercial applications for high-performance composites emerged, including sporting goods, commercial aircraft, and various industrial applications. As a result, DoD usage, which dominated U.S. requirements in the 1970s and 1980s, became a smaller part of the total market. In 2003, the historic and unsustainably low prices observed for carbon fibers were $5.25 per pound for a standard-modulus (32

[1] Composites are commonly denoted by their fiber-matrix composition. A carbon-epoxy composite will consist of carbon fibers in an epoxy matrix.

Mpsi) fiber and $17 per pound for an intermediate-modulus (42 Mpsi) fiber. The DoD market was just under 10 percent of the total U.S. market and 4 percent of the world market.

Military usage is a decreasing share of the total U.S. carbon fiber market—from 43 percent in 1989 to 9 percent in 2003. Because the military usage in the total market is ever smaller—currently less than 4 percent of the world market—the installed integrated capacity in North America is adequate to supply all projected DoD needs for the next decade. In addition, the fiber modulus and strength properties of current production meet DoD's performance requirements for the near term. For the suppliers, this increasingly tight market is expected to lead to pricing structures that could support sustainable reinvestment. For the buyers, in cases where DoD relies on a sole source, prices could remain high.

Significant demand from DoD combined with a technological design shift toward lighter-denier products is expected to strain existing capacity for structural organic fibers. Additional military and homeland security applications are also emerging. In particular, the demand for organic fibers is currently high to satisfy the military's need for body armor and crew protection kits for tactical vehicles. This demand is predicted to remain high for 2 years and then decrease gradually.

### *Fiber Technology*

A few companies continue to invest in new carbon fiber technologies. This investment has been primarily in process improvements and better manufacturing controls to decrease variability and reduce cost rather than to improve properties. Because of this trend, any change in carbon fiber properties is expected to be evolutionary, not revolutionary. Any impact of new lower-cost technology is at least 10 years away.

In the organic fiber area, M5 fiber has the potential to become a commercial fiber with a step improvement in functionality, especially to address the need for optimized structural and ballistic properties of interest to DoD. M5 has the potential to meet the future structural and ballistic needs of the Army. Existing fibers, such as Kevlar, have good ballistic properties but poor properties in compression. M5 could be an enabling technology for a new generation of soldier protection systems.

Finally, although significant progress has been made in improving fiber and matrix properties and reducing material costs, similar progress has not been achieved in manufacturing technology and innovative design to lower the cost of composite structures. Composite processing remains a major opportunity for improvement.

## CONCLUSIONS AND RECOMMENDATIONS

Accelerating technology transition has been identified as a key target.

- One method to speed new fiber technologies to market, especially for such new fibers as M5® or nanocomposite fibers, would be for DoD to provide a guaranteed initial purchase order if the pilot product meets specified property and price requirements.
- In the near term, DoD should provide significant funding to purchase M5 fiber and rapidly evaluate its properties and applications.

Cost reduction has been identified as a key target.

- A clearly significant way to reduce fiber costs over the next 10 years is to reduce or modify the aerospace specifications and qualification process. The DoD should review existing and new qualifications and material specification documents and reduce testing and quality requirements where possible.
- To reduce acquisition costs, all major DoD programs that use fiber or prepreg should have two qualified sources.
- To reduce manufacturing costs in aircraft structures, DoD should invest in manufacturing technology and innovative design concept development. Promising ways to improve dimensional tolerance and reduce processing variability include investment in new continuous process controls that would contribute to controlling fiber structure and purity, prepreg properties such as fiber weight per unit length, and overall property variability.

- To reduce manufacturing costs across all DoD applications, DoD should initiate a program with university-industry-government participation. Promising manufacturing and design concepts should be assessed, including vacuum-assist resin transfer molding (VARTM) to replace more costly manufacturing processes. Virtual manufacturing and simulation should play an important role in accelerated insertion of materials and processes into DoD systems. Research in automation using simulation, sensing, and control systems should be pursued to advance this process from prototype to a production-ready process.

Improved understanding has been identified as a key target.

- The DoD should take a lead in developing a better design methodology that incorporates variability and stochastic aspects of local properties into lifetime models. DoD personnel should use this improved understanding to develop new design allowables and parameters that prevent overdesign of parts and overspecification of fiber properties.
- The DoD should aid in developing a better understanding of new promising technologies in such areas as micron-scale fibers with nanoscale structure and new sizings with the ability to maximize structural and ballistic properties.

# Appendixes

# Appendix A

# Common Acronyms

| | |
|---|---|
| AFRP | aramid fiber reinforced plastics |
| ARL | Army Research Laboratory |
| ARO | Army Research Office |
| ATP | automated tow placement |
| CAD/CAE | computer-aided design and computer-aided engineering |
| CFRP | carbon fiber reinforced plastics |
| CTA | Collaborative Technology Alliance |
| DARPA | Defense Advanced Research Projects Agency |
| DFARS | Defense Federal Acquisition Regulation Supplement |
| DoD | Department of Defense |
| FAA | Federal Aviation Administration |
| FCS | Future Combat System |
| GFRP | glass fiber reinforced plastics |
| ILSS | interlaminar shear strength |
| ISS | interfacial shear strength |
| kpsi | thousand pounds per square inch |
| LCP | liquid crystalline polyester |
| LOI | limiting oxygen index |
| MALDI | matrix-assisted laser desorption/ionization |
| Mpsi | million pounds per square inch |
| MURI | Multidisciplinary University Research Initiative |
| MWNT | multi-walled nanotubes |
| NFT | New Fiber Technology |
| NRC | National Research Council |
| OFW | Objective Force Warrior |

| | |
|---|---|
| PAN | polyacrylonitrile |
| PBO | poly(*p*-phenylene-2,6-benzobisoxazole) |
| PBZT | polyphenylene benzobisthiazole |
| PE | polyethylene |
| PIPD | poly{2,6-diimidazo[4,5-*b*:4',5'-*e*]pyridinylene-1,4-(2,5-dihydroxy)phenylene} |
| PMC | polymer matrix composite |
| RTM | resin transfer molding |
| SACMA | Suppliers of Advanced Composite Materials Association |
| SAF | special acrylic fiber |
| SAMPE | Society for the Advancement of Materials and Process Engineering |
| SWNT | single-walled nanotube |
| UHMPE | ultrahigh-molecular-weight polyethylene |
| UV | ultraviolet |
| VARTM | vacuum-assisted resin transfer molding |

# Appendix B

# Committee Members

**John W. Gillespie, Jr.,** is director of the University of Delaware Center for Composite Materials. He is also a professor in both the Department of Materials Science Engineering and the Department of Civil and Environmental Engineering at the university. Dr. Gillespie currently leads three DoD centers of excellence in composites. He serves as editor for the *Journal of Thermoplastic Composite Materials* and is a member of several professional societies and boards. Dr. Gillespie holds eight U.S. patents and has authored more than 500 technical publications.

**Jon B. DeVault** is currently an independent consultant with extensive knowledge of the carbon fiber industry. Prior to this, he was an executive at Aldila Materials Technology Corporation and at Fiberite, Inc. Before joining Fiberite, Mr. DeVault spent 3 years at the Defense Advanced Research Projects Agency, where he was responsible for planning and implementing a strategy to reduce the cost of polymer matrix composite structures. Earlier in his career, he was president of the Composite Products Group, Hercules Aerospace Company—the largest supplier of graphite materials to DoD and a major manufacturer of composite structures. He has been a member of the Suppliers of Advanced Composite Materials Association (SACMA), the Society for the Advancement of Materials and Process Engineering (SAMPE), and the American Defense Preparedness Association. Mr. DeVault received the SACMA Material Leadership Award in 1996.

**Dan D. Edie** is the Dow Professor in the Department of Chemical Engineering and director for the Center for Advanced Engineering Fibers and Films at Clemson University. His research has focused on the formation, modification, and characterization of carbon, ceramic, and polymeric fibers and composite materials. This research includes both innovative experimental work and theoretical modeling. Dr. Edie has served as a consultant to the U.S. government and industry in the area of high-performance fibers and has served on the editorial board of the journal *Carbon*. Dr. Edie is a past president of the American Carbon Society and has been awarded the Graffin Lectureship by the society. Dr. Edie holds seven patents and has authored more than 150 technical papers and eight book chapters.

**Vlodek Gabara** is the DuPont Fellow in Advanced Fiber Systems at E.I. du Pont de Nemours and Company. His research has focused on the chemistry and technology of high-performance fibers with aramids, such as Kevlar and Nomex, and advanced organic fibers. Dr. Gabara has more than 50 internal DuPont publications and more than 30 publications in the open literature.

**Thomas J. Haulik** is business manager at Cytec Carbon Fibers, LLC. His primary responsibilities at Cytec are to develop and implement market plans and strategies for carbon fiber for aircraft, aerospace, and other high-performance areas. Mr. Haulik joined Cytec when the company acquired the carbon fibers and engineering thermoplastics businesses from BP Amoco in 2001, which had previously acquired it from Union Carbide Corporation. He had been with Union Carbide since 1981. Mr. Haulik has been

involved in several different capacities with SAMPE. In 2002-2003, he served as the SAMPE International president.

**John L. Kardos** is the Lucy and Stanley Lopata Professor in the Department of Chemical Engineering and the Materials Research Laboratory at Washington University in St. Louis. His research efforts have been in the area of composite materials, including structure-property prediction, interface modification, process modeling, and material characterization. He has served a consultant to the U.S. government and industry in the area of reinforced plastics and has served on the editorial boards of the *Journal of Applied Polymer Science*, *Composites Science & Technology*, and *Polymer Composites*. Dr. Kardos has also received the Materials Engineering and Sciences Division Award of the American Institute of Chemical Engineers. Dr. Kardos holds one U.S. patent and has authored more than 120 technical papers and five book chapters

**Linda S. Schadler** in a professor of materials science and engineering at the Rensselaer Polytechnic Institute. She received her doctorate degree in materials science and engineering in 1990 from the University of Pennsylvania and held a postdoctoral research position at IBM's T.J. Watson Research Center before joining the faculty at Drexel University as an assistant professor. She joined the Rensselaer faculty in 1996. She is a winner of the Bradley Staughton Teaching Award from ASM International and the American Society of Engineering Education Dow Outstanding New Faculty award for the St. Lawrence section. Dr. Schadler also has a strong interest in education and participates in outreach and education programs for high school students and teachers, and research programs for undergraduates.