

BIOLOGICAL AND SYNTHETIC HIERARCHICAL COMPOSITES

Creators of high-performance synthetic composites hope to emulate nature by designing materials that are optimized for their ultimate functions on every scale from the molecular to the macroscopic.

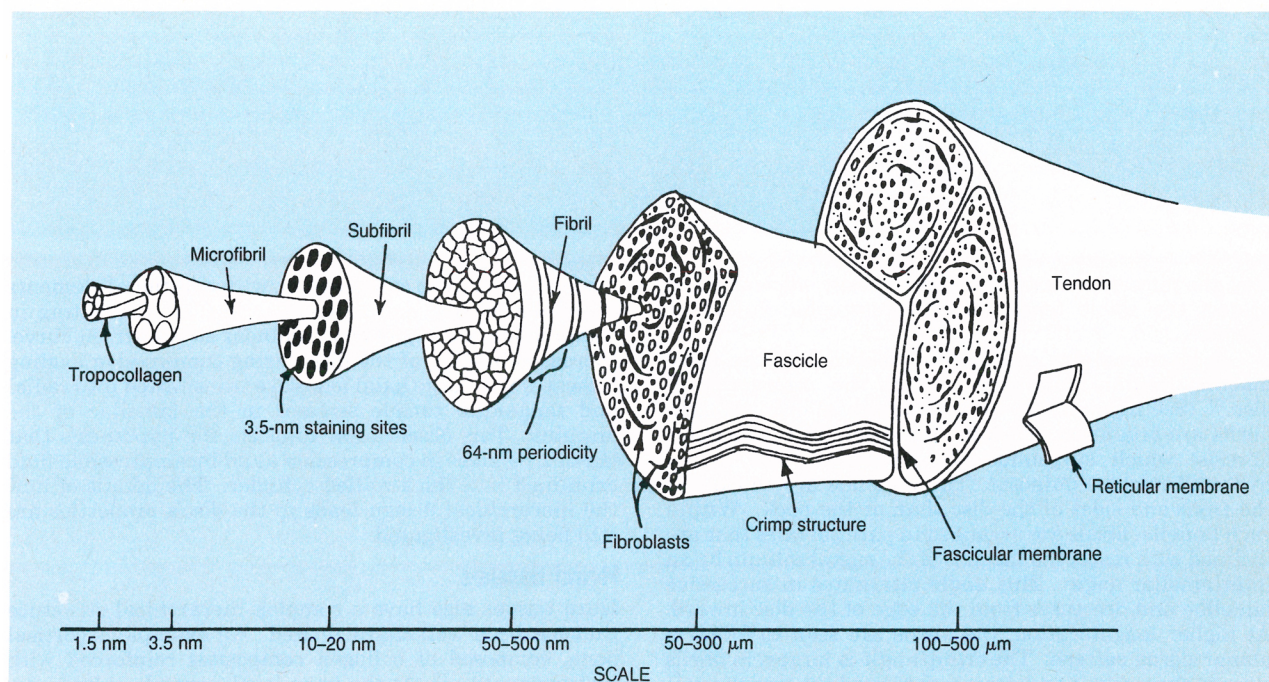
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Many advanced composites can best be described hierarchically. In particular, the biological composites that occur in organisms are generally seen to be organized on discrete scale levels ranging from the molecular to the macroscopic. At each level the components are held together by specific interactions and organized in a way that is optimized for the ultimate function and performance of the overall system. Biological composites typically consist of fibers made from long macromolecules, organized into different structures. One can learn much from biological composites by considering the relationship between their structures and their properties. Whether natural or synthetic, for a composite system to function efficiently its components must be assembled into a specific architecture that gives the required spectrum of properties.

In the arena of synthetic high-performance composites, the hierarchical approach is just starting to be used. At present, synthetic composites are not designed on every scale level. Nature, of course, operates within a different set of constraints than do technology and industry. Trees, for example, have taken millions of years to evolve and can take hundreds of years to grow. Nevertheless, in the future, composite technology will increasingly imitate life as well as it can within the economic constraints of industry.

We will illustrate the lessons learned from biosystems with a few typical examples. Then we will compare them with the state of the art in synthetic continuous-fiber composites, which are made of fibers bundled or woven into structures that are then glued together by a variety of polymeric matrices. Such materials have extremely good properties along the direction of the fibers, although their transverse properties are not always as good as those of other types of composites, such as particulate, flake or chopped-fiber composites.¹⁻⁴ Continuous-fiber composites have applications ranging from prosthetic devices to the skins of supersonic aircraft.



Hierarchical organization of tendon has six levels from the molecular to the macroscopic scales. (Adapted from ref. 3.) **Figure 1**

Biocomposites

Whether from the animal or the plant kingdom, natural composites are designed to withstand complex stresses. A living system must function in difficult environments without suffering debilitating damage. It would appear that Nature always designs efficient composite materials as an integral part of the architecture.

Studies of soft or hard collagen-based connective tissues in animals and of structural celluloses in plants always reveal a hierarchical structure.^{5,6} Starting from very complicated yet similar macromolecular designs and, in the hard tissues, additional commonly occurring inorganic solids, the structures are assembled into distinct and totally different systems. Each system is designed to serve highly specific functions; that is, the composite material is shaped into a unique structural system.

It is tempting to suggest that all of these systems follow what we call the three "rules for complex assemblies." The first rule says that the structure is organized in discrete levels or scales. Usually each level consists of fibrils that are themselves composed of smaller microfibrils and nanofibrils. The fibrils are arranged in layered structures that reflect the specific functional requirements of the overall system. The minimum number of discrete levels or scales observed thus far in biocomposites is four. That is, virtually all biocomposite systems are found to have distinct structural levels at the molecular, nanoscopic, microscopic and macroscopic scales.

The second rule says that the levels are held together by specific interactions between components. Considerable evidence indicates that strong surface-to-surface interactions occur, caused by intermolecular covalent bonds at specific active sites and by van der Waals forces for specific arrangements of inorganic crystals at the nano scale.⁷ An example of the latter occurs in hard materials such as bone, in which hydroxyapatite, a form of calcium carbonate, crystallizes in a specific arrangement on collagen molecules. Whatever the nature of the bonding

between levels, adequate adhesion is required to give the system structural integrity.

The third rule says that these highly interacting fibers and layers are organized into an oriented hierarchical composite system that is designed to meet a complex spectrum of functional requirements. Nature makes very different systems out of similar macromolecular constituents by the process of differentiation during development. Furthermore, as composite systems increase in complexity, they are capable of functioning at higher levels of performance. The so-called intelligent materials and adaptive composite systems result from this type of complex architectural arrangement. A hierarchical biocomposite is more than just a material out of which larger objects can be built. Rather, it is a complete structural system in itself.

These rules can best be illustrated by a few typical examples. Tendon, which connects muscle and bone, is a classic hierarchical system. It is subjected almost exclusively to uniaxial tensile stresses along its length.⁸ Figure 1 shows six discrete levels of organization of the hierarchical structure of tendon.⁹ Beginning at the molecular level with the triple-helical tropocollagen macromolecule, progressively larger and more complex structures are built up on the nano- and microscopic scales. The macromolecules aggregate during biosynthesis to form nanoscale microfibrils, which in turn are packed into thicker discrete subfibrils. The subfibrils form fibrils, in which a characteristic 64-nm banding pattern can readily be seen with an electron microscope. These basic building blocks form a tendon fascicle. At the fascicular level, the wavy or crimped form of the collagen fibrils can be seen with an optical microscope. Two or three fascicles packaged together by reticular membranes form a tendon. This multilevel organization makes a tendon tough and gives it nonlinear, reversible tensile properties. (See figure 2.) If the tendon is subjected to excessive stresses, individual elements fail at different levels of the hierarchical structure. In this

way, the numerous elements absorb energy efficiently and protect the whole tendon from catastrophic failure or fracture.

A more complex soft system composed of the same macromolecular building blocks is the intervertebral disc.¹⁰ (See figure 3.) In an intervertebral disc, collagen fibrils are organized into lamellar sheets in the annulus fibrosis, which surrounds the gelatinous and highly hydrated nucleus pulposus. The lamellae are thicker at the front and sides of the disc than at the back. Within each lamella, fibrils are arranged in parallel lines that are inclined with respect to the axis of the spinal column by an interlamellar angle. This angle alternates in successive lamellae and decreases from the edge of the disc inward. At higher magnification, the fibrils are seen to follow a planar zigzag pattern. The crimp angle is largest in fibrils close to the nucleus and decreases toward the periphery.¹¹

Intervertebral discs absorb shock under complex stresses and permit motion in the spinal column. They are

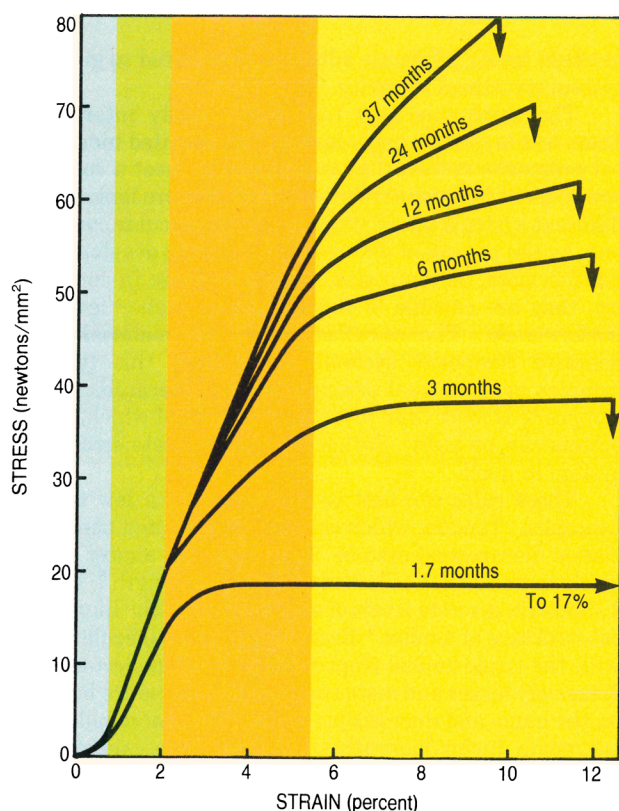
loaded primarily in compression, with additional elements of torsion, flexion and extension. Mechanical testing in compression again yields a nonlinear stress-strain curve. Increased bulging of the disc during compressive loading indicates that large axial loads are transmitted into radial and tangential tensile stresses in the lamellae of the annulus. This observation supports the hypothesis that the disc behaves in compression as an incompressible fluid contained in a thick-walled cylinder. The details of how the hierarchical design leads to the disc's properties are still being investigated.

Hard tissues

Hard tissues also have a complex hierarchical structure that has been well characterized. An example is cortical bone, composed of collagen composites reinforced with hydroxyapatite.¹⁰ At the nano level, crystals of hydroxyapatite with some lattice imperfections have been shown to interact with specific sites of collagen-like macromolecules.⁷ The hierarchical architecture of bone is responsible for its highly anisotropic and viscoelastic mechanical properties. Perhaps the simplest hard biocomposites that demonstrate the rules of hierarchical systems are mineralized structures of invertebrates, such as mollusk shells.¹² Figure 4 shows the highly ordered "brick and mortar" layered architecture of the nacre of abalone.¹³ The bricks are microscale aragonite platelets and are glued together by a structural protein containing polysaccharides. This nano-scale layer of glue reinforces the predominantly inorganic composite shell. The design of mollusk shells makes crack travel difficult: A relatively large amount of energy is absorbed during crack propagation because the cracks run tortuously between the layers. Crack growth can be arrested by organic ligaments bridging the cracks and by sliding of the inorganic platelets, which imparts large plastic deformations to the glue layer. Bridging and sliding are controlled by the chemical and physical properties of the glue, which is itself a complex protein-based material.

Similar structural concepts are observed in plants. They exhibit the same type of scaling and sophisticated architecture as animals. Figure 5 shows the structure that gives trees their mechanical integrity.¹⁴ The organization ranges from the macro scale of macrofibrils imbedded in an amorphous matrix down to the molecular scale of β -D-glucose.

In more complex organisms the composite materials take on more functions. For example, the collagenous intestine wall is designed to undergo large, reversible biaxial deformations while transporting gastric fluids. Here the composite material is simultaneously a container and a pump.¹⁵ Another example is the cornea, which changes shape under mechanical stresses without losing its transparency. The accurate orientation of uniform nanometer-scale-diameter collagen fibers in microscopic layered arrays controls these fascinating mechano-optical properties. One might say that this composite system is tuned to remain transparent.¹⁶ One can easily understand the new term "smart materials" by considering these lessons from nature, and biomimetic materials—



Rat tendon in extension has four distinct regions of stress-strain behavior: a reversible nonlinear toe region (blue), a linear region (green) and two yield regions (orange and yellow), where large-scale irreversible deformation occurs prior to fracture (arrows). The elastic properties of the tendon change with the age of the rat. (Adapted from ref. 3.) **Figure 2**

materials that imitate biomaterials—are now being synthesized based on these lessons, using relatively crude analogs of the biological systems.

Nature designs around potential problems in the life of an organism. For example, stress risers—locations where a structure is particularly sensitive to stress—are minimized by carefully constructed openings in the overall system. The eye socket, for instance, is far more complex than a hole drilled in the skull. Joints are self-lubricating and virtually frictionless. The composite material and the overall system always form an integral design. *The composite is the system; the system is the composite.*

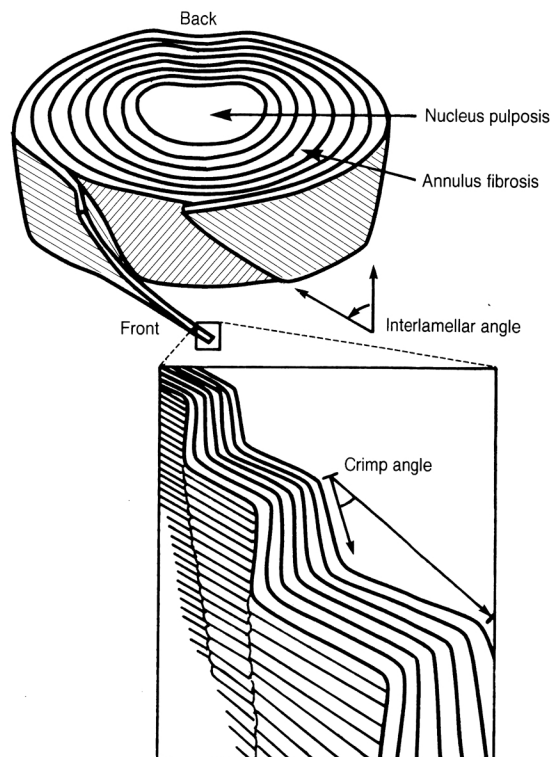
Synthetics

When comparing biocomposites with synthetic continuous-fiber composites, it is instructive to compare the components from which these systems are constructed. The fibers in biocomposites are themselves composite fibers made up of microfibers with surfaces that contain both polar and nonpolar regions. Although we have more fibers to choose from in constructing synthetic composites, these fibers are not designed as composite fibers, and their surface properties are relatively primitive. This is because they are assembled from macromolecular constituents that have a relatively simple structural chemistry.

Figure 6 plots the specific tensile strength (the tensile strength divided by the density) against the specific Young's modulus (tensile modulus divided by density) for a variety of commercial high-performance fibers. Conventional organic materials, metals and inorganic fibers fall near the horizontal axis and are inadequate for the uses envisioned for advanced composites. The advanced light-composite industry developed as a result of the emergence of fibers such as graphite, polyphenylene terephthalamide (produced by Du Pont as Kevlar) and polyethylene (produced by Allied Signal as Spectra).

Just as the fibers of a biocomposite are more complex than their synthetic counterparts, so too are the connective matrices that bind them. However, in the world of synthetic composites, today one can choose from a wide variety of thermoplastic and thermosetting polymer matrix materials. (Thermoplastic materials soften when heated and reharden when cooled, while thermosetting materials harden permanently when heated.)

In synthetic continuous-fiber composites, the fibers are processed into a tow, or a bundle of separate fibers, which contains up to 10^4 fibers. (See figure 7.) Considerable fiber misalignment is often found within a tow. In the final product the matrix resin may not wet the fibers effectively in these regions of misalignment. Such imperfections can cause premature failure and other breakdowns. The tow is processed into uniaxially oriented sheets or other shapes, which exhibit high stiffness and strength in the fiber direction. Panels with good mechanical properties in two dimensions can be constructed by stacking uniaxially oriented fiber sheets with the fibers aligned at various angles. (See figure 8.) Separate tows can be braided to form larger textile structures. Braided systems can have good properties in all three directions. Usually the system is impregnated with liquid resin after

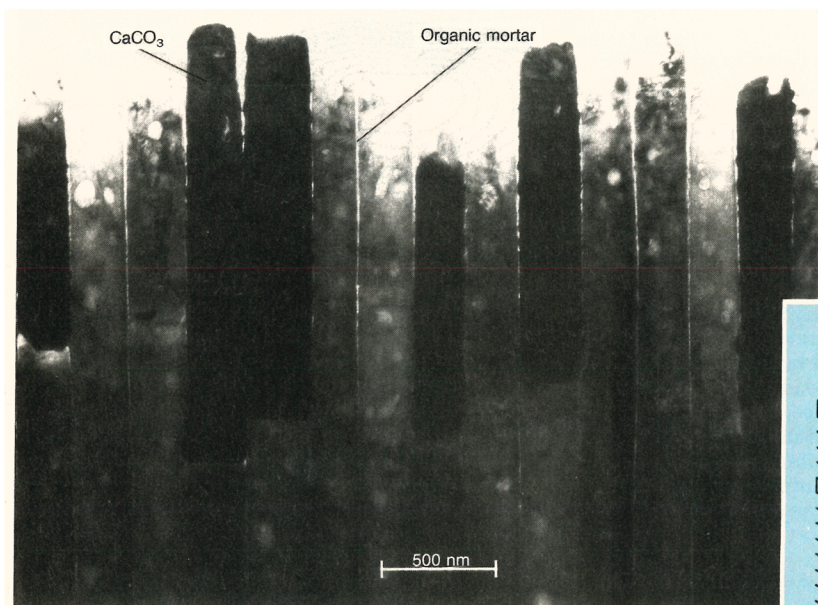


Intervertebral disc is hierarchically organized into lamellar sheets of oriented, crimped fibers that are wrapped around the soft, gelatinous nucleus pulposus. **Figure 3**

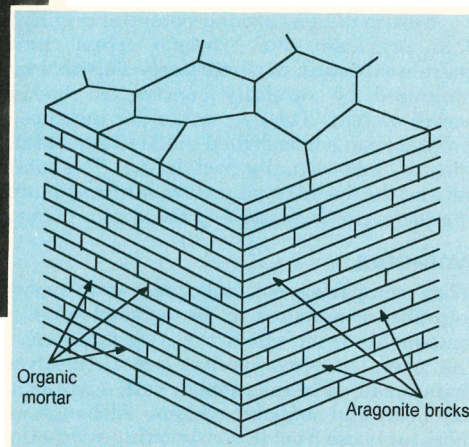
Critical technologies for future advanced composite applications

Scale level	Materials development	Processing and fabrication	Performance
Molecular and macromolecular aggregates		1	2
Single fiber		3	
Polymer matrix	3	3	2,3
Fiber-matrix interface	3	3	2
Fiber tow and fabric	4	1,3,4	4
3-D fiber tow composites and shaped systems		1	2,3

Key: 1, fast, economical composite processing.
 2, durability characterization and enhancement.
 3, compression-resistance enhancement.
 4, fiber tow and fabric structure.



Nacre of red abalone shell (*Halitotis refescens*), imaged here by transmission electron microscopy (left), has a brick-and-mortar structure. The bricks are CaCO_3 (aragonite) platelets, and the mortar is a composite of macromolecules, including structural proteins and polysaccharides, that form a thin film around the platelets. The three-dimensional structure is depicted below. (Courtesy of Mehmet Sarikaya, University of Washington.) **Figure 4**



the textile structure is formed. At this point the system is called a “pre-preg.” Finally, the resin monomers react chemically to form a cross-linked glass matrix within the textile structure.

All synthetic continuous-fiber composites are designed as linear elastic systems and have outstanding stiffness-to-weight characteristics.¹⁻⁴ In addition, these systems have complex failure and fracture properties under fatigue and impact. For example, Kevlar 49 fibers under tension split at a 1° angle along their axis, a process that absorbs a large amount of energy.

Today's world of advanced synthetic composite materials contains numerous examples that can be described with the hierarchical language. However, these systems are relatively primitive and highly imperfect in comparison with biocomposites. The use of high-performance polymer-matrix fibrous composites has increased considerably over the last two decades. The most common commercial composites consist of high-strength, high-modulus fibers such as carbon or Kevlar in a cross-linked thermoset or thermoplastic polymeric matrix. These materials were used initially in military aircraft skins and later in other aerospace applications such as rocket motor casings. Finally they were applied to nonmilitary aircraft, sports equipment, prosthetics and other commercial uses.¹⁷

Further growth of fibrous composites into new commercial applications, however, is limited by materials processing and performance: The polymer impregnation of the fiber bundles and the formation of a macroscopic pre-preg structure from the fiber tows is a relatively slow, costly process. Also, a mismatch between the thermal coefficients of expansion of the fiber and the polymer matrix can cause strains to be frozen into the composite, diminishing its mechanical properties.¹⁸

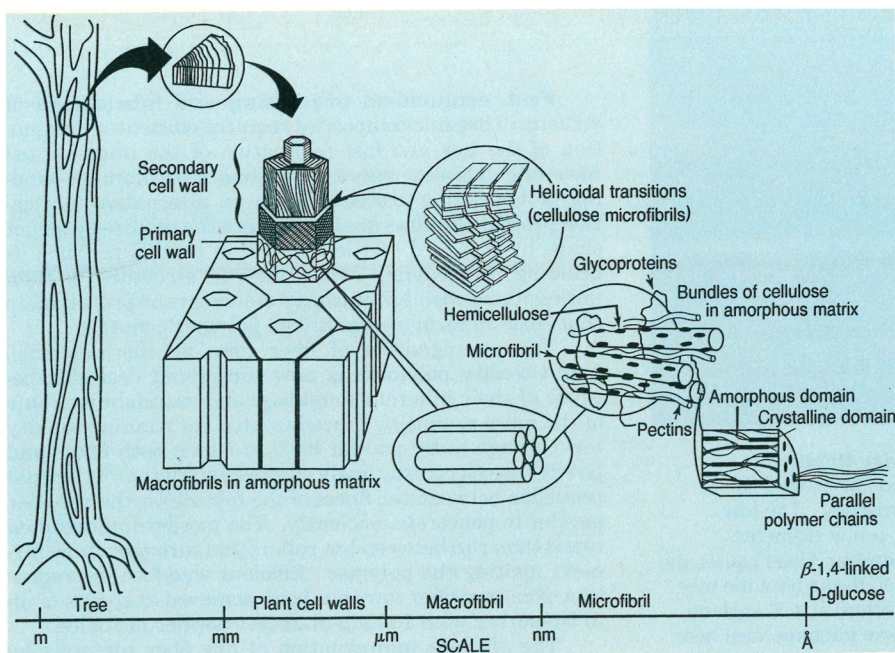
Despite exhibiting excellent mechanical properties in the fiber direction, the composites have poor transverse properties. The mechanical strength of a uniaxial composite is two orders of magnitude lower in the transverse direction than in the fiber direction. These strength limitations can result from crack propagation in the matrix, between the fiber and the matrix, or through the

fiber itself. Poor transverse composite layer properties can cause the composite sheets to delaminate under bending forces. (See figure 9.) Also, the resistance to longitudinal compression in these highly oriented uniaxial composites is an order of magnitude lower than their resistance to tension: Poor bonding between the fibers and the matrix allows fibers to slide past each other and buckle cooperatively at low strain levels. Although they may have very good properties in one or two directions, the composite architectures are usually too primitive for structural applications where the composite is exposed to complex stress fields such as combined tension, compression and torsional forces. Such stresses typically cause failure at the fiber-matrix interface, which leads to a complete breakdown of the system.

Critical technologies

More sophisticated hierarchically structured composites designed for optimum performance at every structural level are required to address these structural deficiencies. The lessons from biology could be used in developing a research and development strategy for the next generation of organic structural composites. Today's poor understanding of the parameters that control the performance characteristics of the polymer-matrix fibrous composites limits somewhat the acceptance of these materials for future applications. The critical parameters that control the failure paths under the synergistic effects of conditions of stress, humidity and temperature over time in a service environment are not well understood. Current testing of materials often looks at only one effect at a time. This lack of understanding, together with the limited amount of long-term composite performance data and standards, has the result that composite structures are overdesigned and users sometimes lack confidence in the overall reliability of the system.

Potential applications for polymer-matrix fibrous



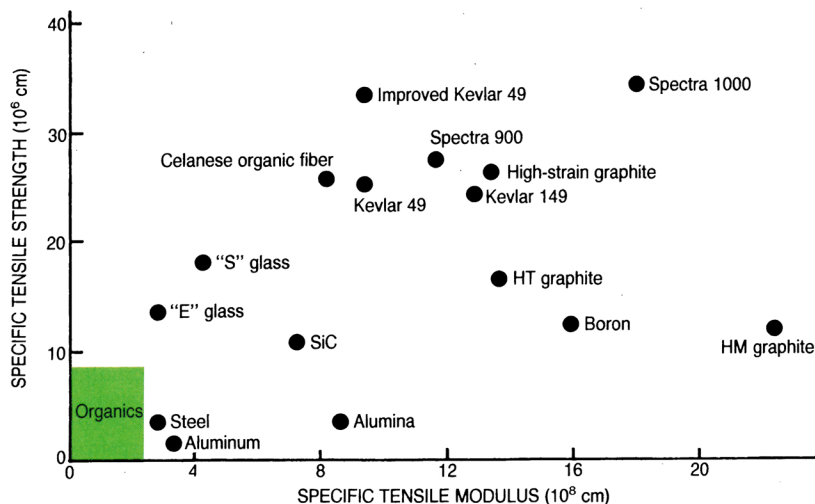
Structural hierarchy of cellulose in wood. (Adapted from a drawing by D. Kaplan, Biotechnology Branch, US Army Natick Research Development and Engineering Center, Massachusetts.) **Figure 5**

composites are broad and include structures for commercial aircraft, automobiles, machines and buildings. One of the most challenging future applications is the proposed use of composites as primary structures in the NASA-funded high-speed civil transport aircraft. In this aircraft cruise speeds of Mach 2.0–2.4 at 60 000 feet are expected to produce skin temperatures of 175–200 °C. The composite materials will have to withstand such conditions for a lifetime of 120 000 hours under mechanical stress.¹⁹

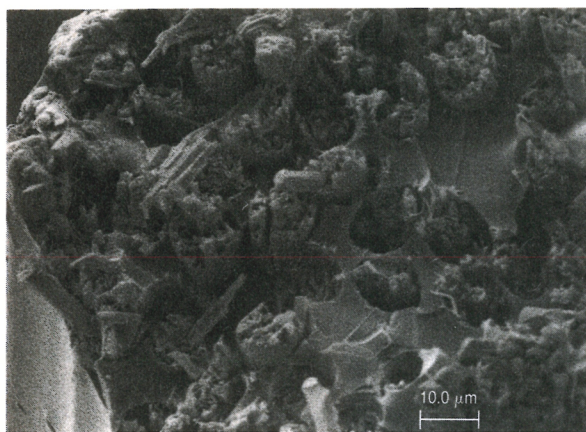
More speculative possibilities are multipurpose materials. These would begin with a single fiber with a C-shaped cross section. Molecules with chosen solid-state properties, such as electrical conductivity or nonlinear optics, would then be encapsulated in the hollow of the fiber. The fiber would be wound into a three-dimensional structure and set in a polymer matrix. Solid-state devices built by such techniques could have many applications. One can imagine houses built of such materials in the far future, in which the walls would display information and channel electricity, heat and light without all of the wiring

and discrete devices required today.

All of the future applications of polymer-matrix fibrous composites require sophisticated materials design and development, economical fabrication and processing procedures, and performance characterization at all scale levels. The goal is to produce both complex-shaped hierarchical structures and standard composite forms such as tubes that can be assembled and disassembled. Disassemblable structures allow one to take apart a structure that has been in use for some years and recycle the components to a lower-performance application. Challenges exist at all scale levels, including the molecular and the nano-scale macromolecular aggregate, the fiber, the matrix, the fiber-matrix interface, the fiber tow and fabric, the pre-preg and the final three-dimensional macroscopic system. The table on page 63 summarizes, for the various hierarchical scale levels, the critical technologies that will enhance the development of future advanced composite applications. We now outline the current state of some of these critical technologies.

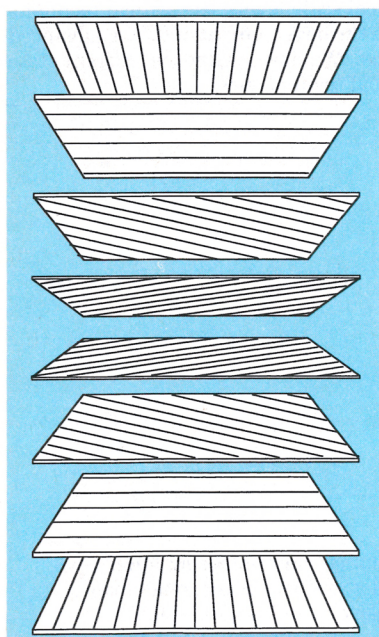


Commercial reinforcing fibers have better mechanical properties than organic materials (green) and conventional metals. **Figure 6**



Fractured tow of Kevlar 49 fibers impregnated with epoxy, as imaged by scanning electron microscopy. The tow contains 267 fibers 12 μm in diameter. Nonuniform spacing between fibers causes the epoxy-poor regions seen throughout the tow. Kevlar fibers usually fracture at a 1° angle to their axis. The transverse fractures seen here can occur if a single bond is broken in each underlying macromolecule. **Figure 7**

Fiber tow and fabric structure. A new technology that is emerging at the fiber tow structural level is the wrapping of a unidirectional tow with another tow of either the same or different chemical composition but having different mechanical properties. This technique allows one to tailor the mechanical response at the tow level to optimize the performance of the macroscopic structure for a given use. For example, one could wrap a ductile material around a stiff one, giving the tow greater ability to absorb energy from impacts. Recently, outstanding polyvinylalcohol fibers have been made that maintain the strength of earlier fibers but have a higher strain to failure. New composite systems using these fibers are being produced.



Stacking of uniaxially oriented tows with the fibers aligned in different directions gives a sheet that has good properties in two dimensions. **Figure 8**

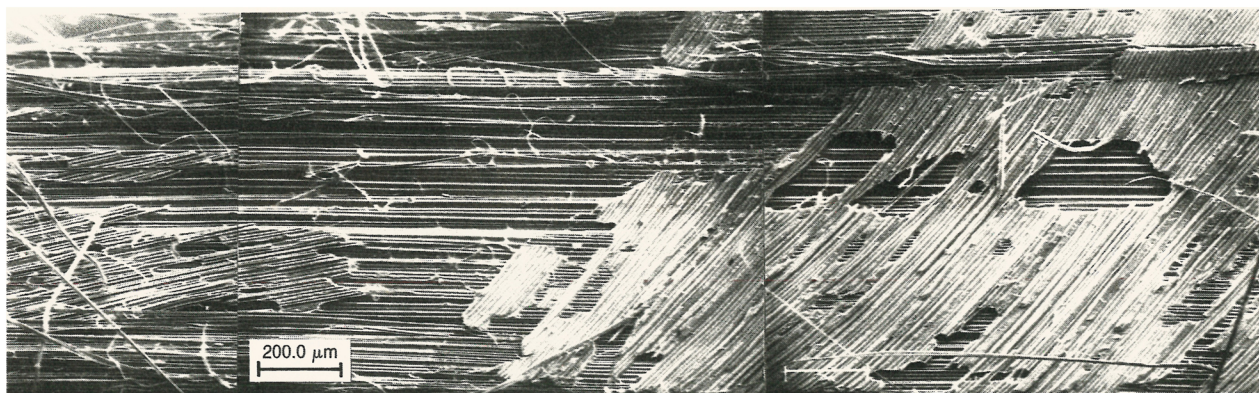
Fast, economical processing and fabrication of structural organic composites requires efficient impregnation of the tow and fast fabrication of the impregnated tows into complex macroscopic shapes by filament-winding or tow-laying procedures. In an alternative fabrication process, dry tows are formed into the required product shape by standard textile fabrication procedures such as braiding or weaving. This preform structure is then impregnated with low-viscosity monomers or prepolymers that react to form a cross-linked polymeric matrix.

The impregnation of fiber tows by thermoplastic, high-viscosity polymers is now considered desirable because of their inherent toughness and recyclability. One of the more promising processes involves running the dry tow through a dry powder bath in which both fibers and powder are electrostatically charged by friction.²⁰ Mutual repulsion between the fibers of the tow allows the polymer powder to penetrate efficiently. The powder-impregnated tow is then run between hot rollers and through a tube furnace, melting the polymer. Efficient void-free impregnation of carbon-fiber tows has been achieved at speeds of up to 30 cm/sec with 100- μm -diameter powder particles.

The efficient impregnation of dry fiber preforms by unreacted thermoset monomers with a minimum of void formation is currently being studied with considerable interest. Critical factors that affect the time needed to impregnate the preform include the effects of vacuum or fill gas, fiber surface chemistry, the liquid pressure at the inlet port and the initial viscosity of the liquid. Recent innovations include a multiple-mold port-injection scheme in which inlet ports are opened in sequence just after the liquid has flowed past each port. This scheme maintains a higher pressure at the liquid flow front during the whole of the impregnation process.

Compression-resistance enhancement. A serious deficiency in high-performance polymer-matrix composites is their relatively poor resistance to compression. Compressive deformation and failure of such composites results from simultaneous cooperative buckling and longitudinal shear slippage in the highly oriented structures in the fibers, in the tows and in the final macroscopic shaped structures. It has been difficult to find ways to disrupt or inhibit cooperative buckling and to increase the resistance to longitudinal shear slippage in typical composites at every dimensional level. Some of the approaches under active consideration to counter cooperative buckling include the use of helically oriented hollow fibers, fibers with a variety of cross-sectional shapes, twisted and wrapped tows, and high-modulus processible resins. Longitudinal shear slippage is being tackled by chemically modifying fiber surfaces to improve the strength of the fiber-matrix interface. At the macroscopic level, an approach to enhancing compression resistance is the introduction of transverse fabrication strains generated by differences in the thermal coefficient of expansion in multimaterial molds.

Characterization and enhancement of durability. Characterization of the critical failure paths of a material requires systematic procedures to identify the types of failure that have the highest probability under periods of exposure to conditions of stress, temperature and moisture. Macroscopic tests must be made that simulate the environment in which the composite will be used. These tests are designed to identify how the composite performs and what its properties are before and after exposure to its service environment. Initial core test programs examine several factors to identify the potential critical failure



Fiber-matrix delamination, shown here in three adjacent scanning electron microscope images of a Kevlar 49-epoxy composite, occurs under impact if the bonds at the fiber-matrix interface are not strong enough. Note the very clean separation between matrix and fibers. **Figure 9**

path and the associated failure mechanisms on all structural levels of the composite. For example, initial tests might determine that hydrolytic degradation and microcracking during processing are important. An accelerated test program then seeks to determine the effect of these combined factors over the composite's service lifetime. Industry as a whole does not yet follow this expensive procedure, and this deficiency has led to unforeseen failures in the aerospace industry in recent years.

A systematic durability test program of this type is now under way for the composites proposed for the high-speed civil transport aircraft. Typical examples of mechanisms of composite damage at each structural level^{1-4,21} have been reported in previous applications. For example, on the molecular level, hydrolysis can break the amide linkage in Kevlar fibers. With only one bond broken per macromolecule, Kevlar becomes brittle, breaking transversely like glass fiber instead of splitting longitudinally. (See figure 7.) On the microscopic level, submicron-sized holes form in the polymer matrices of moisture-laden composite specimens when they are exposed to high temperatures where the local water vapor pressure exceeds the polymer cavitation stress. On the macroscopic level, impacts can cause large-scale delamination between uniaxial composite layers. (See figure 9.)

There is no doubt that ideally synthetics should be designed at every scale level. Then one could hope to incorporate some of the lessons learned from biocomposites. For example, for a hierarchically designed synthetic a partial breakdown at one level or between levels may not necessarily mean that the system will fail in service. However, industry is only beginning to consider the structure in detail at every level. Clearly such an approach is extremely challenging and at present can't be justified for every application.

A realistic goal is the computer modeling of the structures of synthetics at every scale level and the development of the processing technology needed to manufacture such materials. By drawing on the knowledge and techniques so acquired, we will be able to design and manufacture compromise materials that are optimized within realistic economic and technological constraints.

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