HANDBOOK OF ADVANCED MATERIALS

ENABLING NEW DESIGNS

Editor-in-chief

James K. Wessel

Wessel & Associates
Oak Ridge, Tennessee

WILEY-INTERSCIENCE

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CONTRIBUTORS

D. C. Agarwal Krupp-VDM Technologies Corp., 11210 Steeplecrest Drive, Suite 120, Houston, Texas 77065-4439

Robert Akid Materials Research Institute, Sheffield Hallam University, Howard Street, Sheffield, United Kingdom S1 1WB

Chris Deemer Energy Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Bldg. 212ET, Argonne, Illinois 60439

William A. Ellingson Energy Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Bldg. 212ET, Argonne, Illinois 60439

F. H. (Sam) Froes Institute for Materials and Advanced Processes (IMAP), University of Idaho, Moscow, Idaho 83844

G. N. Haidemenopoulos Department of Mechanical and Industrial Engineering, University of Thessaly, Volos, Greece

Michael G. Jenkins Department of Mechanical Engineering, University of Detroit Mercy, 4001 W. McNichols Rd., Detroit, Michigan 48219

J. Randolph Kissell The TGB Partnership, 1325 Farmview Road, Hillsborough, North Carolina 27278

John U. Knickerbocker IBM, Inc., 208 Creamery Road, Hopewell Junction, New York 12533

Sarah H. Knickerbocker IBM, Inc., 208 Creamery Road, Hopewell Junction, New York 12533

Syros G. Pantelakis Department of Mechanical Engineering and Aeronautics, University of Patras, Patras, Greece

Theodore P. Philippidis University of Patras, Department of Mechanical Engineering and Aeronautics, Patras, Greece

Ivar E. Reimanis Metallurgical and Materials Engineering Department, Colorado School of Mines, Golden, Colorado 80401

David W. Richerson Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112

Chris A. Rudopoulos Materials and Engineering Research Institute, Sheffield Hallam University, City Campus, Sheffield, United Kingdom S1 1WB

John Shaffer Oak Ridge National Laboratory, P.O. Box 2009, Oak Ridge, Tennessee 37831

Vinod Sikka Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, Tennessee 37831

Anastasios P. Vassilopoulos University of Patras, Department of Mechanical Engineering and Aeronautics, Patras, Greece

James K. Wessel Wessel & Associates, 127 Westview Lane, Oak Ridge, Tennessee 37830

Eric Whitney Pennsylvania State University, State College, Pennsylvania 16804

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PREFACE

The use of improved materials enables engineers to design new and better products and processes. Benefits include increased sales of improved products and, where new materials are used in manufacturing, reduced plant cost. Society benefits through the use of improved products that use these new materials.

Sophisticated new materials save lives (artificial hearts, shatterproof glass, bulletproof vests), conserve energy (lightweight cars) and expand human horizons (aircraft, spacecraft, computers through the World Wide Web). In the twenty-first century a new generation of materials promises to again reshape our world and solve some of the planet's most pressing problems. Although there is a tremendous array of materials, this book focuses on so-called advanced materials, especially those offering the latest advancements in properties. They are materials of construction with exceptional properties enabling improvement in the engineering components or final products in which they are used. They are also the latest in revolutionary materials and the latest improvement in more traditional advanced materials.

As a designer of "hardware," you may be tempted to assume that the best material for your use is the one you have been using. If so, you will find that this book includes many common materials of construction that have seen recent improvements. For the more adventuresome, we include revolutionary materials whose use may result in great benefit, enabling unique and cost-effective product design.

This handbook presents the most recently introduced advanced materials in an effort to inform you as soon as possible of materials that may improve your product or process. Each chapter describes material characteristics from which materials can be tentatively selected for further exploration. Additional information is available from the references, engineering societies, and trade associations. Examples include The Composite Fabricators Association, The United States Advanced Ceramic Association, ASM International, The American Society of Mechanical Engineers, The Aluminum Association, The American Iron & Steel Institute, The Steel Manufacturers Association, International Titanium Association, and others. All are available through their websites.

This book's purpose is not to provide all the data you need to select materials. Each chapter describes an individual class of materials. Most include corrosion-resistant data plus a separate chapter on this important property. The book's purpose is to narrow your material selection. For your final decision, work with the material supplier as a partner, sharing your problem's parameters. Material suppliers have broad experience that will benefit your material selection. Treat them as a joint problem solver rather than a vendor. Be open to a design change that will realize the benefits of using a new material. Always test materials before use.

Some of the materials presented have revolutionary performance compared to the existing materials that you are using. Others are improvements over existing materials, but, unlike revolutionary materials, they are more familiar, with abundant engineering data, and some similarity to your existing material. Revolutionary materials, like continuous fiber ceramic composites (CFCCs), offer a breakthrough in performance in extreme environments like superior resistance to high temperature, corrosion, and wear. Others, including CFCCs, are also stronger and lighter weight.

Some of the materials presented are high priced, reflecting their high performance. They are used where the result economically benefits the provider and the user. Life-cycle costing will reveal if this is true for your application.

Designing a product involves selecting a material, shape, and manufacturing process. Finding an optimal combination of these to maximize performance and minimize cost is essential for innovation in engineering design and education.

Psychologists tell us that 5% of designers are willing to try something new and 80% will follow if the 5% are successful. Be one of the 5%. The use of new materials can save money, reduce downtime, reduce maintenance, increase operating temperature, increase efficiency, lower emissions, and reduce life-cycle costs.

James K. Wessel
Oak Ridge, TN

CHAPTER 1

Polymer Composites

JOHN SHAFFER*

Oak Ridge National Laboratory, P.O. Box 2009, Oak Ridge, Tennessee 37831

THEODORE P. PHILIPPIDIS and ANASTASIOS P. VASSILOPOULOS†

University of Patras, Department of Mechanical Engineering and Aeronautics, Patras, Greece

*Sections 1.1–1.7
†Sections 1.8–1.13

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1.A POLYMER COMPOSITES

1.1 DESCRIPTION

1.1.1 Scope

Polymer composites can cover a broad range of material combinations. For this chapter, we will consider those combinations that are between the stages of those still being invented and those in wide use. We will also restrict our consideration to those combinations that are intended for structural application. Many, if not most, of the basic concepts and principles of use will be applicable across the total range of materials developed. The specific characteristics of the materials discussed or used as examples will be of those that are advanced in the sense that their full use potential has not yet been realized. For that reason, a great deal of attention will be given to those material combinations that incorporate continuous carbon or graphite fibers as a reinforcing material in a high-performance polymer matrix. Unlike many metals, polymer composite formulas are often proprietary to their suppliers. Contact the supplier to determine the best polymer composite for your application. Suppliers can be identified by contacting the Composite Fabricators Association at `www.cfa-hq.org`. They are located at 1010 North Glebe Road, Suite 450, Arlington, VA 22201, telephone 703-525-0511.

1.1.2 History and Future Developments

Modern polymer composites can trace their origins back to the 1950s when researchers at Wright-Patterson Air Force Base in Ohio began to investigate the properties of plastics that had within them embedded glass fibers. The motivation for these investigations was the search for materials that would meet the ever-increasing demands for higher performance aircraft. Lighter, stronger, and stiffer were the guiding principles. In conjunction with companies such as Owens-Corning Fiberglas and Union Carbide, a high-performance composite of continuous S-Glass and epoxy was developed. This composite found applications in such places as the Poseidon missile casing and ballistic armor. It is still an important material today.

In the 1960s, fibers composed of oriented carbon or graphite began to be developed. The fibers were of low density and higher stiffness than glass fiber. As the demands of agencies such as the Air Force and National Aeronautics and Space Administration (NASA) grew for higher stiffness materials than metal or glass fiber composites, these carbon/graphite fibers and their composites became the materials of choice. Today, many consider *advanced composites* to be those reinforced with carbon or graphite fiber. In actuality, glass-fiber-reinforced composites continue to find new, advanced uses. The design, manufacturing, testing, and performance measuring methods for polymer composites containing any fiber were developed during the time when glass-reinforced composites were finding expanded usage.

The history of glass and carbon-fiber-reinforced composite development is documented by several authors. It is not the intent here to review that history beyond the simple introduction given above. It needs to be pointed out, however, that the composites developed as a result of the search for stiffer, lighter, stronger has had some fortunate side effects in other areas. The new materials also gave the designers more choices of materials for their electrical, thermal, and corrosion needs. These nonstructural properties will be further explored later in the chapter.

The future of polymer composite development is mixed. The decade of the 1990s has seen a slowdown in the drive for improvements led by aerospace. Companies that competed with each other in the need to produce ever more advanced products have seen the market drastically change. Performance used to be the differentiating factor. In today's world, performance with affordability or value is the key. The industry is looking for new customers in application areas that were not even imagined when advanced polymer composites were developed. Golf clubs, tennis rackets, hockey sticks, softball bats, pole vault poles, canoes, fishing poles, and the like are but the tip of the iceberg for new applications. Automobile, truck cab and trailer, railroad car, and ship applications are under active development. The success of these applications will depend upon designers embracing these materials in their work.

As inventors and applications engineers begin to be comfortable with the type and nature of these advanced materials, application areas will expand and costs will come down. It is hoped that this chapter will give to the designer the basic knowledge and understanding of how these material work, how they are made, and, most importantly, how they can open design imagination.

1.1.3 Definition

Stating a simple definition of a composite is a deceptively complex task. It gets even more difficult if the definition is intended to convey the multitude of options available. Here are a few examples:

1. Made up of distinct parts or elements
2. A macroscopic combination of two or more distinct materials, having a recognizable interface between them
3. Two or more materials judiciously combined, usually with the intent of achieving better results than can be obtained by using individual materials by themselves
4. High-strength fiber—primarily continuous, oriented carbon, aramid, or glass rather than randomly distributed chopped fibers or whiskers—in a binding matrix that enhances stiffness, chemical and hydroscopic resistance, and processability properties

Each of these definitions is equally correct. They express an increasing degree of complexity to the product being defined. They also imply the ability (or difficulty) to define a material simultaneously with its application. *Engineered materials*, as they are often called, now require the designer to consider materials other than those available to him in the "handbook." The material he will use is now his to define, as he needs. This material will be made from parts and elements put together in a manner chosen to best fulfill the need. The possibilities are immense; the solutions only limited by imagination.

1.2 CONSTITUENT MATERIALS AND PROPERTIES

The materials that make up the parts of a composite are usually referred to as the constituents. For a polymer composite, the two basic parts are the polymer matrix, or resin system, and the fiber reinforcement. In the next section, the options available for each of these two parts will be presented along with some specialized intermediate forms of product that form the starting point in the design of a structure made from a polymer composite.

1.2.1 Fibers

Polymer composites have developed into important structural materials due to the wide variety of reinforcing fibers that are available. Glass and carbon fibers are by far the most common types and are produced by a number of manufacturers worldwide. Other fiber materials such as aramid, quartz, boron, ceramic, or polyethylene are also available and provide unique properties. For applications in advanced polymer composites, the most common form of the fiber is continuous tow (carbon) or roving (glass). In this form, continuous filaments have been gathered as untwisted bundles and packaged in spool form. Typically, these packages weigh between 2 and 20 lb and are supplied on 11 by 3-in. cores. This product is the basic element for further processing (either directly or via intermediate forms) into a polymer composite structure.

Carbon fibers were first commercially produced from a regenerated cellulose fiber (rayon). Because of high production costs and environmental concerns, rayon-based carbon fiber is not widely used today. The majority of carbon fiber available today is made from an acrylic precursor fiber (polyacrylonitrile, or PAN) and is the most commonly used structural fiber. Fibers made from petroleum or coal tar pitch are also available and, because of their high modulus and unique thermal properties, find uses in thermal management applications. PAN-based carbon fibers are available from a number of sources. Tables 1.1, 1.2, and 1.3 present typical properties of carbon fiber products. The tables are grouped by tensile modulus grade; low or standard (33–35 Msi), intermediate (40–50 Msi), and high (>50 Msi).

Today, new fiber developments are producing material with heavier tow count and lower costs. These materials are usually of the low modulus type and will find applications in high-volume applications such as automotive, construction, and infrastructure.

TABLE 1.1 Low Modulus (<275 GPA) Carbon Fibers

Supplier	Trade Name	Designation	Tensile Modulus (GPa)	Tensile Strength (GPa)	Elongation (%)	Density (g/cm^3)
Toray	Torayca	T300	230	3.53	1.5	1.76
		T300J	230	4.21	1.8	1.78
		T400H	250	4.41	1.8	1.80
		T700S	230	4.90	2.1	1.80
BP Amoco	Thornel	T300	231	3.75	1.4	1.76
		T300C	231	3.75	1.4	1.76
		T650/35	255	4.28	1.7	1.77
Hexcel		AS4	228	4.07	1.8	1.79
		AS4C	231	4.15	1.8	1.78
		AS4D	241	4.28	1.8	1.79
SGL Carbon	Sigrafil C	C10	180–240	2.00	1.0	1.75
		C25	215–240	2.50	1.05–1.40	1.78
		C30	220–240	3.00	1.25–1.60	1.78
Grafil		34–700	234	4.48	1.9	1.80
		34–600	200	4.00	1.7	1.79
Zoltek	Panex	33 (45K)	228	3.79	1.5	1.80
Toho Rayon	Besfight	G30–400	235	3.80	1.6	1.76
		G30–500	235	3.92	1.7	1.76
		G30–700	240	4.81	2.0	1.76
Fortafil		F3(C)50K	227	3.80	1.7	1.80
Nippon	Granoc	XN-20	200	2.73		
		HT	230	4.80		

TABLE 1.2 Intermediate Modulus Carbon Fibers

Supplier	Trade Name	Designation	Tensile Modulus (GPa)	Tensile Strength (GPa)	Elongation (%)	Density (g/cm^3)
Toray	Torayca	T800H	294	5.49	1.9	1.81
		T100G	294	6.27	2.2	1.80
		M35J	343	4.70	1.4	1.75
		M30	294	3.92	1.3	1.80
Hexcel		IM7	276	5.45	2.0	1.78
		IM8	303	5.73	1.9	1.79
		IM9	276	6.00	2.2	1.79
Grafil	Pyrofil	MS40	345	4.83	1.3	1.77
		MR50	296	5.52	1.9	1.80
Toho Rayon	Besfight	G40-600	295	4.51	1.5	1.74
		G40-800	285	5.79	2.0	1.80
		G50-500	345	2.94	0.9	1.79

TABLE 1.3 High Modulus Carbon Fibers

Supplier	Trade Name	Designation	Tensile Modulus (GPa)	Tensile Strength (GPa)	Elongation (%)	Density (g/cm^3)
Toray	Torayca	M40J	377	4.41	1.2	1.77
		M50J (6K)	475	4.12	0.8	1.88
		M60J (6K)	588	3.92	0.7	1.94
BP Amoco	Thornel	P55S (4K)	379	1.90	0.5	2.00
		P75S (2K)	517	2.10	0.4	2.00
Hexcel		UHM	440	3.73	.08	1.87
Grafil	Pyrofil	HS40	455	4.41	1.0	1.85
		HR40	393	4.83	1.2	1.82
Toho Rayon	Besfight	G55-700	380	4.90	1.2	1.79
		G80-600	540	3.82	0.7	1.92
		G100-300	650	3.33	0.5	1.97
Nippon	Granoc	HM	377	4.40		
		XN60	600	3.50		
		YS95A	920	3.53		

Other types of fibers are used in polymer composites and impart special properties. Table 1.4 lists many of these along with typical properties and uses. See Chapter 3 for a more thorough description of these fibers.

1.2.2 Resins

Polymer composites get their name from the type of matrix or binder used to hold the fibers together to make a solid material of designed properties. The most important function of the polymer matrix is to allow the fibers to share the loads. This requires that the matrix be more flexible than the fiber and be attached in

TABLE 1.4 Miscellaneous Fibers

Fiber Type	Manufacturer	Trade Name	Tensile Modulus (GPa)	Tensile Strength (GPa)	Density (g/cm^3)	Uses
PBO	Toyobo	Zylon AS	180	5.8	1.54	Ballistic protection, sailcloth,
		Zylon HM	270	5.8	1.56	High-temperature filters
Boron	Textron		400	3.6	2.57	Bicycle frames, skis, aircraft repairs
Quartz	Quartz Products	Quartzel	78	3.6	2.2	Radomes, heat shields, high-temperature applications
Ceramic	Nippon Carbon	Nicalon	193	2.9	2.55	High-temperature applications
Aramid	DuPont	Kevlar	55–143	2.3–3.4	1.44–1.47	Armor, ballistic protection
Polyethylene	Allied-Signal	Spectra	86–103	2.1–2.4	0.97	Chemical resistance, impact properties

some manner to the fiber. While the method used to manufacture the composite (to be discussed later) can have a large influence on the effectiveness of the loading transfer, reinforcing fibers are usually sold with a *sizing*, or coating, on them specifically designed to promote chemical bonding between the matrix and the fiber surface.

The matrix also serves as a coating or protector for the fibers and must therefore be chosen not only for its ability to work with the fiber as the load transfer medium but also for its environmental performance. Polymer matrices can be divided into two general classifications: thermoset and thermoplastic. As their names imply, heat is used during processing. A thermoset material is generally processed as a liquid and crosslinked, or cured, through the application of heat to form a nonreversible chemical structure. In contrast, a thermoplastic is melted, formed and then cooled in a reversible process wherein the materials are not crosslinked. There are even materials, such as the polyimides, that exhibit characteristics of both types.

The field of polymer chemistry is very broad. Many excellent reference books exist that detail the molecular structure, processing, and performance of polymers. In this section, only property information on the most common types of polymers used as composite matrices will be presented.

Thermoset matrix materials include epoxies, polyesters, bismaleimides, polyimides, cyanate esters, and phenolics. Epoxies are by far the most common matrix material for advanced polymer composites. Table 1.5 lists major types of matrix materials available, their physical properties, and service limits.

The curing of a thermoset material usually requires the use of a hardener or catalyst in order to promote the crosslinking process. Three types of materials are common for crosslinking epoxies: amines, anhydrides, and Lewis acids. Each

TABLE 1.5 Matrices for Advanced Polymer Composites

Resin Family	Typical Cure Temperature (°F)	Maximum Service Temperature (°F)	Typical Tensile Properties		
			Strength (ksi)	Modulus (ksi)	Elongation (%)
Epoxy	350	350	8–13	375–500	3–7
	350	300			
Phenolic	300	300	1.0–1.6	75–150	
Bismaleimide	375	450	11.9	620	
Cyanate	180	350	12.7	470	

type of curing agent will modify the physical properties of the polymer and can change the processing methods. Matrix suppliers will assist in the choice of materials and processes for a given application.

Thermoplastic matrix materials differ from thermoset in that they are not crosslinked materials that require hardeners and heat. Thermoplastic materials are solids that are formed to shape by heat and pressure. When combined with a fibrous reinforcement, the composite is pressed or molded into the final desired shape. The differences in manufacturing methods can sometimes result in savings of time and equipment cost. Property differences in the final product exist and are usually the determining factor in the selection of the resin type. Many types of thermoplastic matrix materials exist. Conventional materials such as polyesters, polystyrene, nylon, and the like are not usually thought of as advanced thermoplastic matrices even though they are widely used in automotive, medical, and other commercial applications.

1.2.3 Prepregs

Composites are manufactured by combining fibers and resin in a mold or on a form that defines the final product shape. This can be done in one step by a wet lay-up method or through the use of an intermediate product known as a *prepreg*. A prepreg is a product form in which the reinforcing fibers are preimpregnated with the polymer matrix resin and partially cured to form a sheet or tapelike material. Many fiber and resin suppliers also supply prepregs. Other companies are just prepreg suppliers. The prepreg allows precise control over the relative proportions of resin and fiber in the composite and allows fiber orientation to be controlled. The development of this intermediate product form has had a large impact on the expanding use of polymer composite structures. While there are generic types of prepregs available, almost any fiber–resin combination is possible. The reinforcements can be contained in the prepreg as parallel fibers (unidirectional), woven fabrics of textile types, nonwoven cloth, or braids. The choice of a particular product form is closely related to the manufacturing process to be used and to the complexity of the final product.

1.3 DESIGN OPTIONS

The preferential incorporation of reinforcing fibers into a polymer matrix opens up the design options available. At one end of the spectrum there are unidirectional fiber-reinforced materials that maximize the use of the available strength and stiffness of the fiber and produce a product that is highly directional in its properties. At the other end are random or multidirectional fiber materials whose properties approach isotropy.

1.3.1 Final Products

Today, advanced polymer composites find their greatest use in the aerospace sector where they were initially developed. Stealth aircraft such as the F-177 and the B-2 are only possible because of the unique properties of advanced polymer composites such as high strength and light weight. From helicopter blades to rocket motor casings to ballistic armor, these materials have fueled a revolution in new product applications. Initially, many projects attempted to replace a metal part with composite parts by direct substitution. This did not often work well. The unique properties of composites could not be incorporated in a part substitution and the resultant product frequently was more expensive than the original. Fortunately, as time passed, designers became more familiar with composite design methodologies and designed new products with composites in mind from the concept stage. The following section outlines the design approach.

1.3.2 Introduction to Methodology

The design of structures with advanced polymer composites proceeds through the application of classical lamination theory. Individual laminae, or plies, are stacked with the fibers oriented in various directions to build a laminate with the desired properties. Designers are used to working with materials such as plastics and metals that are described as homogeneous and isotropic. That is, the materials properties are not dependent upon the position or orientation in the material. For these classes of materials in a plane stress state, the relationship between stress and strain is described through the elastic constants Young's modulus E, and Poisson's ratio, ν.

However, a laminated composite material cannot usually be accurately described this simply. Homogeneous orthotropic, homogeneous anisotropic, heterogeneous orthotropic, and heterogeneous anisotropic are additional descriptions that may be required to accurately analyze a laminated material. Fortunately, this complexity is not often required and, with the advent of modern software, is even manageable on desktop computers. For the balance of this section, we will make the assumption that a composite exhibits homogenous orthotropic behavior. We will also consider a special ply configuration that approaches isotropic behavior—quasi-isotropic.

1.3.3 Laminae

As indicated previously, a homogenous, isotropic material requires two independent constants to describe its stress–strain behavior. A homogeneous, orthotropic composite material has three perpendicular planes of material property. If the axes are chosen to coincide with the reinforcing filament direction, then this set is called the principal lamina direction. Dimensionally, these laminae are physically thin compared to their length and width. Although the thickness stresses are small and as applied in a laminated structure, a state of plane stress or plane strain is assumed. This leads to the need for four independent elastic constants in order to describe the stress–strain response: E_{11} and E_{22}, Young's modulus; G_{12}, shear modulus; and ν_{12}, major Poisson's ratio. This description of a lamina, or ply, is most common in the design of a laminated composite structure. Testing of ply materials is most oriented toward establishing these constants.

1.3.4 Laminates

When multiple layers of lamina are combined and act structurally as a single layer, a laminated composite is created. To analyze a laminated composite structure, the designer must know the properties of each layer and how the reinforcing fibers are oriented with respect to one another, that is the stacking sequence. For example, a laminate consisting of 16 individual layers may have the fibers oriented in the following fashion:

Two layers with fibers at 0°
Two layers with fibers at 90°
One layer with fibers at +45°
Three layers with fibers at −45°
Three layers with fibers at −45°
One layer with fibers at +45°
Two layers with fibers at 90°
Two layers with fibers at 0°

This description is quite lengthy and shorthand methods have been developed to present the information:

$[0_2/90_2/45/-45_3/-45_3/45/90_2/0_2]_T$ or
$[0_2/90_2/45/-45_6/45/90_2/0_2]_T$ or
$[0_2/90_2/45/-45_3]_S$

Each of these methods describes the laminate. In the first method, each of the orientations is given along with the number of layers indicated by the subscript. The [ ]'s and the subscript T indicate that this is a description of the total laminate. The second method simply combines the two −45° layer groups into one. The third description, however, recognizes an important property of this particular lay-up sequence. It is symmetrical about the centerline of the laminate. Only one-half of the stacking sequence is explicitly listed, and the subscript T is replace by S to indicate the symmetry. While lamination theory can accurately analyze any stacking sequence, the condition of midplane symmetry is an important one for the designer of polymer composite structures. Nonsymmetrical lamina lay-up can result in out-of-plane bending and twisting under mechanical or thermal stress that must be considered.

In addition to midplane symmetry, there is one other design concept that is usually followed by designers. That is, the stacking sequence is usually "balanced." This means that there are an equal number of plies at angles of $+\theta$ and $-\theta$. Construction that follows this convention will avoid the shear coupling that is present in a single orthotropic lamina.

Lamination theory describes the stress–strain response of stacked orthotropic lamina. This behavior can be used to analyze the strength of the laminate if the assumption is made that the basic strength criteria for the lamina remain valid in the laminate. Under this assumption, a strength analysis proceeds by determining the individual ply stresses and/or strains in the laminate and comparing them to the allowable for the ply. Failure is often deemed to have occurred when one of the plies exceeds an allowable stress–strain limit. This *first ply failure* does not necessarily lead to complete failure of the laminate, as the failed ply may transfer some or all of the load it carried to another ply in the laminate and not exceed an allowable at that location. Procedures are available to analyze *ply-by-ply failure* sequences but are usually used as part of a failure analysis process rather than a design study.

A final word on composite laminate and ply failure. Since a fiber-reinforced lamina is modeled most frequently as an orthotropic material, the use of a failure criteria such as the maximum principal strain criteria used with isotropic materials is not applicable. A maximum strain criteria for an orthotropic material requires that the strains developed under load be referred to the lamina principal axes and evaluated against the tensile and compressive allowable for the lamina. This leads to the need for five failure strains; tensile and compressive limits in the fiber direction, tensile and compressive limits in the transverse to the fiber direction, and an in-plane shear limit. Other failure criteria, such as the Tsai–Wu criterion, are developed as yield surfaces that depend upon the interaction between the lamina principal direction and shear yield strengths. Commercial computer software for analyzing laminated composite structures is available. These packages can be customized to allow input of new materials, modified failure limits, and failure analysis methods.

1.4 TESTING/ANALYSIS

1.4.1 Mechanical Properties

The mechanical properties of polymer matrix composite materials depend upon the type of fiber and resin used, the relative percentages of each, the laminate lay-up, and the method of manufacture. The properties presented in this chapter are focused upon the fiber and resin materials that make up the composite. These are the product forms most often purchased by a user who combines them into a laminate. In this section, the methods used to determine the constituent and laminate properties commonly used in selecting materials will be reviewed.

The fiber properties presented in the previous tables are typical of what a potential buyer will encounter. The tensile strength, tensile modulus, and elongation are usually determined by the impregnated strand test. Over the past few years, industry standard test methods have been developed for determining these properties. The properties are, thus, reasonably comparable between manufactures in a general sense. The test is also useful for quality control purposes.

Fiber density is an important property. Often it is specific strength or modulus that controls the applicability, especially in weight and stiffness critical areas. There are also industry standards that can be used to measure this property.

The important properties of the polymer matrix resins used in advanced composites are both chemical and mechanical. For uncured thermoset resins, the important properties are related to the processing method to be employed. Viscosity, gel time, cure temperature, and the like all must be considered in order to properly process and cure the composite. The test methods used are common in the polymer manufacturing business and can be found in many references.

One of the most important properties of a cured thermoset resin is the glass transition temperature (T_g). This parameter is both a measure of the completeness of the cure and an indication of the maximum service temperature of the composite. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) are two common techniques. DSC measures the amount of heat given off (or absorbed) in a resin sample as the temperature is increased. When the T_g no longer changes the resin is completely cured. With the DMA technique the response of the resin to mechanical stress is monitored with respect to temperature. The temperature at which a significant change to the elastic moduli is observed is the T_g. Since these methods measure two different parameters, they can give two different estimates of T_g. Care should be taken when reviewing supplier data as the method used is not always indicated.

As prepregs are an intermediate product from that combines fiber and resin in a specific ratio and partially processes the resin, it is important to know that the ratio and the “b-staged” resin are properly prepared. The fiber–resin ratio is measured by the aerial weight, or in grams per square meter, of fiber. Since this property is chosen by the application requirements, it is not a handbook type of quantity. A typical value for this parameter will place the fiber fraction at ~60% by volume.

In the cured laminate, the calculation of the relative amounts of fiber and resin is an important measure of the quality and proper processing history of the material. ASTM methods are available for determining these ratios and for determining the void content. Void content can have a detrimental effect on the properties of the composite and is usually limited to 1 or 2% of the material’s volume. The technique involves burning (in the case of glass fiber) or chemically digesting (in the case of carbon fiber) the resin matrix. The relative weights (W) of fiber and resin, when combined with the densities (D) of the composite (C), fiber (F) and resin (R) will yield the void content:

$$V_v = 100[1 - D_C/W_C(W_R/D_R + W_F/D_F)]$$

The tensile properties of an advanced polymer composite material are usually measured with a flat coupon. ASTM D3039 is one test method standard that can be used. The test is applicable to unidirectional and oriented laminates. It differs in purpose from the impregnated strand test previously discussed. The structural fiber–resin ratios are more closely represented in the coupon test, and the results are more applicable to the actual planned use. The influences of the matrix and fiber-to-matrix interface are more evident. Testing at elevated temperatures and after exposure to other environmental conditions often use this specimen. ASTM methods also are available to govern the procedures used.

Compressive properties of polymer–matrix composites are difficult to measure. The ASTM provides a recommended method but many users develop their own. Again, the purpose of compressive testing is often to evaluate the performance of a fiber–resin combination to various service environments. Numerous tests for shear properties have been developed. A shear test is often used to measure the effectiveness the fiber–resin interface. The ASTM, again, provides methods to follow. A simple test such as ASTM 2344, apparent interlaminar shear strength, is often used for quality control and comparative purposes. ASTM D3518 is a procedure for measuring shear strength and modulus design data.

1.5 NONDESTRUCTIVE TESTS (QUALITY ASSURANCE)

Nondestructive tests of polymer matrix composites have received a great deal of attention. The difficulty and expense of performing destructive tests on actual structures have spurred the search for testing techniques that verify performance (quality assurance) without destroying the product. While no standard nondestructive tests for product quality exists, the use of ultrasonic techniques have become quite sophisticated. The ability to detect delaminations, inclusions, and voids on complicated geometries has made the test routine easier in many programs. Similarly, the use of infrared thermography to detect flaws or damage has developed recently.

1.6 ENVIRONMENTAL PERFORMANCE

1.6.1 Temperature

The service or operating temperature of a polymer matrix composite is probably the most important parameter considered in choosing the chemical nature of the matrix. In Table 1.5, the glass transition temperature, T_g, is an indication of the maximum service environment. The operating temperature is kept below the T_g. Polymer matrix composites are limited to 260°–316°C (500–600°F) applications.

Above these temperatures, metal or ceramic matrices are required. Testing for temperature effects is usually done by performing several of the mechanical tests previously described at elevated temperature. In general, tests that stress the matrix, such as shear and compression, will show the greatest effect. Temperature effects are generally reversible provided that the temperature exposure has not been high enough to cause physical damage to the matrix.

1.6.2 Moisture Exposure

Moisture tends to “plasticize” or soften the matrix. As with temperature effects, the composite properties are measured after exposure to water for varying times and at varying temperatures. Moisture effects, like elevated temperature effects, are generally reversible.

1.7 FABRICATION

1.7.1 Methods and Processes

1.7.1.1 Overview

The manufacture of a composite structure requires that the constituent fiber and resin be combined in a specified ratio, with the fibers in a chosen orientation and heated to cure or form the final product. The details of how this process is accomplished will ultimately determine the properties of the composite structure. Many of the techniques used have evolved from processing knowledge for plastic molding. Indeed, in the automotive sector, the composites manufacturing methods used most frequently are termed *liquid molding* and are similar to the resin transfer molding process used in the aerospace sector. The principal difference is the speed requirements for the product. And therein lies the challenge for modern advanced composites. The tolerable cost of manufacturing is dependent upon the end use. Low-volume application areas, such as aircraft or space, typically utilize the more expensive methods, and high-volume areas, such as automotive or infrastructure, require that costs be low. The processing methods that will be outlined in this section will follow manufacturing evolution from manual, labor-intensive methods to highly automated and rapid methods.

1.7.1.2 Processes

Manual Lay-up The simplest technique used to make a composite structure is the manual lay-up method. Fibers are laid on a form and liquid resin is added and distributed throughout the fibers by hand rolling. After the desired thickness is attained, the product is allowed to cure, either at room temperature or in an oven. This method is time consuming and produces composites of low quality. Much effort has been undertaken in the industry to improve the manual lay-up method. The development of prepreg materials was a significant advancement. Better control of the fiber–resin ratio and simpler lay-ups, combined with autoclave curing, produced better parts. Figure 3.15 shows the Filament winding technique used for composites.

Automated Tape Laying New machines have been developed that aid in the lay down of prepreg. These tape-laying machines are programmed to follow the contours of the mold, laying down prepreg tape in prescribed orientations and applying heat and pressure automatically. The head can follow reasonably gentle contours and, with some models, can automatically add or drop tape layer. The lay-up usually still requires vacuum bagging and autoclave curing.

Filament Winding The filament winding process can be a very cost-effective method for producing a composite part. As its name implies, the method consists of wrapping fibers around a mandrel in layers until the desired thickness is reached. A winding machine allows the fiber orientation to be varied thereby allowing the composite part to develop the design property profile. Matrix curing is most often done in an oven, although autoclave curing is occasionally used.

Resin Transfer Molding In resin transfer molding (RTM), a mold is filled with reinforcement and injected with resin. Cure takes place in the mold and the composite takes the shape of the mold. There are variations on this basic technique depending upon how and when the fiber and reinforcement are combined and cured. Reaction injection molding (RIM), structural reaction injection molding (SRIM), vacuum-assisted resin transfer molding (VARTM), and resin film infusion (RFI) are types that have been developed, usually first for a specific part need.

Pultrusion Pultrusion is the process where bundles of resin-impregnated fibers are cured by pulling them through a heated die. The addition of glass or carbon fiber to the pulling process yields a product that maximizes strength and stiffness in the pulling direction. When combined with part rotation and overwrapping techniques, pultrusion can produce a wide variety of structural composite shapes.

1.7.1.3 Tools

Advanced composites are formed on tools. The preceding process illustrations contain tooling adapted for the composite forming method used. Pressure and cure/forming temperatures are primary drivers for the design and materials chosen. Production quantity is also an important factor in tooling selection. Composites, themselves, are often used as tooling materials. As the cost of raw materials comes down, manufacturing costs, tooling, and speed became the barriers to the introduction of an advanced composite part into a high-volume application.

Machining The machining of polymer composites differs from both the machining of metals and plastics and requires consideration of techniques used in both.

TABLE 1.6 Adhesive Bonding vs. Mechanical Fastening

Property/Performance	Adhesive Bonding	Mechanical Fastening
Stress concentration/delamination	×	
Peel strength		×
Bearing Strength	×	
Ease of construction		×
Environmental performance		×
Disassembly		×
Cost	×	

Composites are usually made near net shape. They usually require trimming, sanding, painting, drilling, grinding, and the like. Composites are weak in the directions transverse to the fibers and are subject to delaminating. Generally, the same types of tools that are used for metalworking can be used. Tooling companies sell special tools designed for composites with specific kinds of reinforcement. Carbon tends to be brittle and Kevlar tough. Tools tipped with carbide or impregnated with diamond flakes are common. Cooling may be necessary to prevent overheating and damaging the matrix material.

Assembly/Joining Adhesive bonding is the most common method used for joining polymer composites. The adhesives used can be one-part or two-part adhesives and cure at room temperature or elevated temperature. The materials are similar to those used for matrix materials and chosen with many of the same considerations in mind. Surface preparation is extremely important to the quality of the bond as is the choice cure cycle. Mechanical fastening uses methods similar to metal joining, that is, rivets, bolts, pins, and the like. Care must be used as a hole will reduce the strength of the composite and increase the potential for delamination. Often, reinforcing pads, doublers, must be used. Fastener materials, especially in carbon composites, can cause galvanic corrosion. Hence, nickel, nonmetal, and titanium are commonly used. Table 1.6 lists some of the property and performance considerations in the choice of assembly method.

1.B FATIGUE OF GLASS-FIBER-REINFORCED PLASTICS UNDER COMPLEX STRESS STATES

1.8 INTRODUCTION

Design allowables of general applicability for fatigue-critical composite structures cannot be easily established. Different material systems, that is, type of reinforcement and matrix, lamination sequence, load cases definition, and geometry of structural component usually result in case-specific situations treated more or less as such. The reason is that aforementioned parameters affect differently a multitude of failure mechanisms, for example, fiber breaks, matrix cracking, debonding, delaminations and the like, that are propagating in a different way and rate. Therefore, what has been observed in the past during the development of a structural composite application is an initial phase with intensive experimental efforts to produce large databases on fatigue strength of specific material systems and a subsequent assessment period in which design allowables, fit to purpose, are extracted. Safety levels are set by design standards and are mainly based on empirical partial safety factor approaches.

Fatigue behavior of carbon-fiber-reinforced epoxies (CFRP) has been extensively investigated the last 25 years due to the concentrated effort in developing composite structural components for aeronautical applications. Most aspects of fatigue-related engineering problems, that is, life prediction, property degradation, joints design and the like, were confronted leading to the adoption of design allowables and large amount of published data, for example [1–5]. Yet, damage tolerance issues have not been treated efficiently [6] due to many reasons, the main one being the lack of definition of a generalized damage metric, for example, such as the crack length in metals, that could be of use with different lay-ups and material configurations [7]. In addition, the effect of variable amplitude loading on remaining life and fatigue under complex stress states have only received limited attention.

Structural response to cyclic loads of glass-fiber-reinforced plastics (GFRP) extensively used in a number of mechanical engineering applications such as leisure boats, transportation cars, and the like, has not been investigated at any significant extent until 15 years ago. Due to the amazing growth of wind energy industry, especially in Europe, much effort was spent the last decade in establishing fatigue design allowables of GRP (glass-reinforced polyester), in particular, laminated composites for wind turbine rotor blades. Lots of experimental data were produced characterizing fatigue strength of matrix systems such as polyester, epoxies, and vinylester reinforced by continuous glass fibers in the form of woven or stitched fabrics and unidirectional roving [8–17]. The effect of both constant and variable amplitude, that is, spectral, loading conditions was investigated.

However, limited experimental data and design guidelines are available of the complex stress state effect, produced either by multiaxial or off-axis loading, on fatigue behavior of GFRP laminates. Existing studies [18–22] point out the strong dependency of fatigue response on load direction, as a result of material anisotropy and indicate the need to continue research on this topic including effects of spectral and nonproportional loading.

Experimental results are presented herein from a comprehensive program consisting of static and fatigue tests on straight edge coupons cut at various on- and off-axis directions from a GRP multidirectional (MD) laminate of $[0/(\pm 45)_2/0]_T$ lay-up. Fatigue behavior of off-axis loaded laminates, that is, complex state of stress in material principal directions, is investigated in depth for several off-axis orientations. This includes derivation of signal–noise (S–N) curves at various R ratios ($R = \sigma_{min}/\sigma_{max}$), statistical evaluation of fatigue strength results and determination of design allowables at specific reliability levels. Constant life diagrams are extracted for the various off-axis directions and are compared with existing data from similar material systems.

Several investigators have been concerned in the past with the multiaxiality of fatigue stresses. Hashin and Rotem [23] first, proposed a fatigue strength criterion for fiber-reinforced plastic (FRP) materials, based on the observed failure modes. For unidirectional materials two distinct failure modes exist, fiber and matrix dominated, respectively, whereas for laminated composites a third mode was introduced to cope with delaminations [24]. To use the criterion, experimental determination of three S–N curves is assumed, that is, axial loading in the fiber direction, transversely to it and shear loading in the principal material directions. Application of the criterion is limited to materials for which failure modes can be separated, that is, it cannot be used for woven or stitched fabrics. Fawaz and Ellyin [25] proposed a multiaxial fatigue strength criterion that needs less experimental data as input, that is, only one S–N curve and the static strength properties. Other authors have also attempted to modify existing static failure criteria to cope with cyclic loads [18, 19, 26, 27].

A quadratic failure polynomial criterion, introduced in [20] to predict fatigue strength under complex stress states, is shown to forecast satisfactorily material response under off-axis and multiaxial loading for all the cases of stress ratio R considered in this study.

Besides strength prediction and fatigue behavior under off-axis loading, stiffness reduction measurements were performed as well. By continuously monitoring force-displacement loops, longitudinal Young's modulus is derived as a function of the number of cycles. Its variation, depending on the applied stress ratio and off-axis load orientation, is modeled by a simple empirical equation [28], which is shown to fit satisfactorily the experimental data. It is observed in general [21, 22] that the higher the cyclic stress range, the lower the stiffness reduction with increasing number of cycles, and this is particularly true for alternating load, $R = -1$ Furthermore, a systematic statistical analysis for all stress ratios, R, and off-axis orientations proved that irrespective of stress amplitude level, modulus degradation data are fitted satisfactorily by standard statistical distributions.

Stiffness degradation measurements for various R values were used to define fatigue design curves corresponding to specific modulus degradation and not to failure. In that case, test points in the S–N plane denote that under cyclic stress, σ, a predetermined stiffness reduction is reached after N cycles. The corresponding, stiffness-controlled, fatigue design curves, denoted as Sc–N, can serve better the requirements of design and full-scale testing of structural components made of FRP materials. For example, in wind turbine rotor blade testing [29], functional failure is said to correspond to irreversible stiffness reduction of up to 10% and therefore, Sc–N based fatigue design of the blade must be used instead to comply with eventual certification requirements.

For the GRP material database presented herein, Sc–N curves were determined and compared to fatigue strength allowables [22]. It was shown that these two families of curves can be correlated, and, therefore, it was possible to derive