

MANUFACTURING OF POLYMER-MATRIX COMPOSITES

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Contents

1. Introduction
2. Applications of Polymer-Matrix Composites
 - 2.1 Automotive Applications
 - 2.2 Marine Applications
 - 2.3 Aerospace Applications
 - 2.4 Construction Applications
 - 2.5 Other Applications
3. Constituent Materials
 - 3.1 Matrices
 - 3.2 Reinforcements
 - 3.3 Preimpregnated Reinforcements
 - 3.4 Core Materials
4. Composite Properties
5. Manufacturing Techniques
 - 5.1 Molds
 - 5.2 Wet Layup
 - 5.3 Prepreg Layup
 - 5.4 Liquid Molding
 - 5.4.1 Resin Transfer Molding
 - 5.4.2 Structural Reaction Injection Molding
 - 5.4.3 Vacuum Infusion
 - 5.5 Compression Molding
 - 5.6 Filament Winding
 - 5.7 Pultrusion
6. Outlook

Summary

Fiber-reinforced polymer-matrix composites offer a range of potential advantages over conventional construction materials, but present challenges in design and manufacturing. This chapter commences with a discussion on application of polymer composites to illustrate where they may be competitive, and then briefly introduces constituent materials and composite properties, whereas the bulk of the article covers the most common manufacturing techniques and their characteristics.

1. Introduction

The term composite refers to a combination of two or more distinct materials into one with the intent of suppressing undesirable properties of the constituent materials in favor of the desirable properties. This definition therefore does not include metal alloys or polymer blends, which are

material combinations on the atomic level. A composite offers a combination of properties that are not available in any isotropic material and is thus a unique material concept in its own right.

The composite concept is not an invention; there is an abundance of naturally occurring composites, such as wood, bone, insect exoskeleton, mollusk shell, and countless others. Natural composites tend to be weaker and less stiff than the synthetic composites that are the main topic of this article, but they are often superior in terms of design and manufacture. Natural composites are “smart materials” in that they adapt to the environment. A tree for example grows in such a way that it becomes stronger in the direction where strength is required and an incurred damage is gradually repaired. The earliest recorded example of conscious human use of the composite concept dates back to the early Egyptians, who used straw to reinforce clay from the Nile to make brick. (There is even a biblical reference to this practice: *Exodus 5:7*.) In the third millennium BC, the Egyptians also made papyrus “paper” from the papyrus reed by placing strands of the reed parallel to each other to form layers, which then were stacked perpendicular to each other in alternate directions; the stack was then allowed to dry under pressure to form the paper-like sheet. Also the Chinese used straw-reinforced brick and in AD 108, invented paper (the word paper is derived from the word papyrus), which is a random, planar arrangement of individual cellulose fibers held together by a binder.

In most load-bearing, or structural, applications, composites consist of a bulk phase enclosing a fibrous reinforcing phase; in conventional terminology these are referred to as matrix and reinforcement, respectively. The objective of the matrix is to integrally bind the reinforcement together and to introduce external loads to the reinforcement, but also to protect it from adverse environmental effects. While the matrix gives a composite its shape, surface appearance, and environmental tolerance, it is the reinforcement that carries most of the mechanical loads and thus largely dictates macroscopic stiffness and strength.

There are numerous man-made examples of the composite concept encountered in everyday life, including paper, particle (chip) board, and reinforced concrete to mention a few, but the most specialized incarnations are those that are the subject of this article. The matrix may be metallic, ceramic, or polymeric in origin. While metal and to a lesser degree ceramic matrices are used in structural composite applications, polymer matrices are by far the most significant and this article is dedicated to polymer-matrix composites. The fibrous composite reinforcement may be discontinuous or continuous and randomly oriented or aligned, see Figure 1. Since the reinforcement is the primary load-bearing constituent, its form and degree of orientation is critical to the macroscopic properties of the composite. The most impressive mechanical properties are found in composites with continuous and aligned reinforcement, see Figure 2.

Figure 1. Schematic of Different Reinforcement Configurations

Figure 2. Fracture Surface of Continuous Carbon-fiber-reinforced Epoxy Composite
The fiber diameter is 7 μm . (Photograph courtesy of Jakob Kutteneuler, Department of Aeronautics, Kungl Tekniska Högskolan, Stockholm, Sweden)

The most common reason why polymer composites are used in structural applications is that they offer a certain property, often stiffness, at a lower weight than alternative materials, which most of the time is a metal, but sometimes also plastic, wood, or concrete. There are numerous other potential advantages of composites other than their excellent structural capabilities, including corrosion resistance, electrical insulation, lower tooling and assembly costs, and many more. It is

however important to realize that these potential advantages assume proper selection of constituent materials and manufacturing technique, otherwise the result may be inferior properties. Table 1 summarizes some of the many potential advantages of composites over more conventional engineering materials as well as common fields of application. It is easy to become impressed with the potential advantages of composites, but the disadvantages must not be ignored. It is probably essentially true that if one disregards cost, a polymer composite can outperform any other engineering material in all respects but temperature tolerance. It is nevertheless rare that cost is not important and one thus has to take into account high raw material cost, lack of knowledge and experience, and challenging manufacturing. Composites are certainly not appropriate in all applications; a critical assessment of material candidates must always be made in terms of performance-to-cost ratio.

Table 1. Potential Advantages of Composites

2. Applications of Polymer-Matrix Composites

Just as with most new materials, the development of high-performance polymer composites has been driven by military, and later aerospace, needs, where performance at least used to be more important than cost. While the search for new and improved materials continues to be driven by military needs and desires, most types of polymer composites have become commodity materials. This transition from specialized to commodity material concept does not mean that improvements in material performance have ceased, but the emphasis of the development has shifted to improvements in design, manufacturing, and ultimately cost, thus reflecting the relative maturity of the concept. While the main developmental efforts in the field of high-performance composites have been military in origin, a largely parallel development has taken place in electrical and boat-building industries. In electrical applications, the interest was spurred by a need for a nonconductive engineering material, whereas composite boats early on were found to have advantages in terms of manufacturing cost, durability, and much reduced need for maintenance.

The international composites market, which is dominated by the US and Europe with approximately equal shares, continues to grow at a healthy pace. Dominating fields of application are transportation and construction, particularly where electrical insulation and corrosion-resistance are valued, followed by consumer products and sporting goods. The following sections discuss the reasons for use of composites in some fields of application.

2.1 Automotive Applications

An important reason for use of composites in transportation applications is arguably to save weight in order to reduce fuel consumption or to increase payload. However, few consumers are prepared to pay a higher price for their new car to reduce operating costs over a number of years, although the trend is nevertheless to reduce vehicle weight. While the structural qualities of composites are seldom valued, there is still a very convincing argument in the possibility for reduction in production cost. Since start-up costs for composites manufacturing generally are an order of magnitude lower than for metals, composites have proven very competitive for vehicles manufactured in short series. Another way to reduce production cost is to integrate what in steel would be several smaller parts into one composite component; far-ranging parts integration may lead to significantly reduced assembly costs. Cost reduction is without doubt the most persuasive argument, but composites also allow greater geometrical complexity than sheet metal, thus allowing a greater design freedom and more appealing vehicle aesthetics.

There are numerous examples of use of composites in automotive applications. Most common are exterior body panels and various components under the hood, such as integrated front ends, battery trays, and protective shields. All such applications have in common that they do not carry substantial structural loads. However, there are some truly load-bearing composite applications, such as leaf springs, drive shafts, pressure vessels for compressed natural gas to mention a few. Use of composites for the primary structure is nevertheless so far very limited, but may be found in self-supporting bodies of extreme sports and competition cars, some buses, truck trailers, and specialty vehicles.

2.2 Marine Applications

Almost all leisure craft—from the smallest dinghy to competition powerboats and sailing yachts—have been manufactured from composites for many years. Clearly the main reason for this dominance is that composite boats are relatively inexpensive. Manufacturing of composite boats is amenable to mass-production and fewer craftsmen's skills are required than to work wood or metal. Start-up costs are generally very low, since few specialized tools or facilities are needed. From the boat owner's point of view it is extremely attractive that a composite boat requires very little maintenance since it does not rot or rust. Indeed, many of the very first composite boats from the 1950s are still in use largely unaffected by the elements.

While the hull of small boats almost always is a single-skin composite laminate, deck and floorboards are often sandwich structures in order to obtain sufficient stiffness. (In this context, a sandwich is a structural element with a relatively weak and light core material interleaved between and integrally bonded to two stiff sheets of material, most often composite laminates. The purpose of using a sandwich structure is generally to obtain high bending stiffness.) In larger boats, sandwich structures tend to be used throughout hull, deck, and floorboards. More recently composites have become the material of choice also in masts, booms, and rigging. Composites have also been used in specialized shipbuilding applications, where low weight and non-magnetic materials are key reasons for use of composites.

2.3 Aerospace Applications

Although aerospace applications are insignificant in terms of production volume, the field has been and still is vital to the development of composites, since the extreme desire to obtain the ultimate in performance has brought us most of our knowledge of composite design and high-performance raw materials. Saved weight in a flying craft directly translates into increased load-carrying capability or performance enhancements and in fighter aircraft such performance enhancements literally may be the difference between life and death. Also in aerospace applications composites may lower manufacturing cost due to the possibility of parts integration.

Common aircraft composites include control surfaces (rudders, flaps, etc.), wing skins and substructures, leading edges, complete vertical and horizontal stabilizers, fairings, engine nacelles, thrust reversers, propellers, radomes, landing gear doors, access doors, and large parts of cabin interior and cargo compartments. While many aircraft composites are single-skin laminates, sandwich components with honeycomb are in extensive use. Modern helicopters make even greater use of composites than aircraft. While rotor blades have been composites for years, an increasing portion of the helicopter structure is made of composite to reduce manufacturing cost and save weight. For spacecraft, gains from weight savings are even greater than in aircraft and efforts to weight-optimize the structures of both payload and launch vehicle are far-ranging, resulting in frequent use of composites. Composites also offer the possibility of designing a structure, such as satellite antennae, with virtually no thermal expansion over a very wide temperature range.

2.4 Construction Applications

This area is by far the biggest consumer of composites, largely due to dramatic improvements over conventional construction materials in corrosion resistance. This has proved a very convincing argument in chemical plants, wastewater treatment plants, harbors, off-shore oil platforms, and other corrosive environments. Many such construction applications employ standardized construction members in full analogy with the use of steel beams. Composites are also used to rehabilitate earthquake-damaged concrete columns of bridges by laterally supporting them with composite jackets. Similar techniques are used to upgrade the load carrying capacity of engineering structures, including bridges. Another emerging composite application area is bridge decks and complete bridges, where gains can be made in speed and ease of erection.

2.5 Other Applications

In electrical applications, the insulating properties of glass-reinforced composites is generally more important than the structural capabilities. Applications in electrical and electronic areas include equipment housings, transformer spacers, and cable trays to mention a few. Tool handles, booms for “cherry picker” trucks, and ladders are common applications. The attraction of eliminating direct electrical contact between electrician and potentially hot wires as well as between electrician and ground is obvious.

Sanitary applications are dominated by shower enclosures, bath tubs, spas, sinks, and cabinets. Related applications include bird baths, fish ponds, small pools, and water slides. In such applications it is mainly the design freedom and the possibility of economically manufacturing short series that are the main advantages.

Sporting goods, including golf clubs, racquets, and skis, are well-recognized and accepted composite applications, but the list of composite sports applications is nearly endless. While there are many reasons for the massive dominance of polymer composites in sports applications, the main ones are fashion, vastly improved performance, lower weight, durability, and in some cases lower cost.

3. Constituent Materials

The materials that make up, or constitute, a composite include at least the matrix and the reinforcement. However, oftentimes the matrix is not homogeneous but mixed with inert fillers, performance-enhancing additives, etc. Likewise, the reinforcement is normally surface treated or coated with some substance to improve properties. With sandwich components the core and the face-core adhesive are additional constituents.

3.1 Matrices

The matrix of a composite has several functions: it is a binder that holds the reinforcement in place, it transfers external loads to the reinforcement, and it protects the reinforcement from adverse environmental effects. Moreover, the matrix redistributes the load to surrounding fibers when an individual fiber fractures and laterally supports the fibers to prevent buckling in compression.

Polymers may broadly be divided into thermoplastics and thermosets. A thermoplastic is solid at room temperature, but melts upon heating. When the melt is cooled, the thermoplastic solidifies. In theory this melting-solidification sequence is infinitely repeatable without any chemical change to the polymer. In reality, each heating cycle degrades the polymer to some extent. Thermoset polymers are usually liquids at room temperature (or following moderate heating) and they solidify

through a chemical reaction initiated by a chemically reactive substance called initiator or hardener. The molecules of thermosets contain features that readily react to form covalent bonds between molecules. In contrast, thermoplastics lack such features and are therefore under normal processing conditions largely inert. The chemical reaction in a thermoset is called crosslinking or cure and it is promoted by increased temperature; indeed, many thermosets require heating to crosslink as intended. Crosslinking eventually results in one gigantic molecule throughout the polymer sample and since this molecular arrangement corresponds to a lower energy state than the random molecular orientation of the liquid, heat is released-crosslinking is exothermal. Since this molecule is bound together by covalent bonds it cannot be melted through reheating.

All polymers are characterized by a temperature region where, if the temperature is increased, the stiffness rapidly drops orders of magnitude, thus rendering the polymer useless from a structural point of view. The temperature where this change is the most rapid is called the glass-transition temperature and may effectively be regarded as the maximum-use temperature of the polymer. For common polymer matrices (both thermosets and thermoplastics) the glass-transition temperature is typically 50–100 °C, although high-performance matrices may have glass-transition temperatures in excess of 200 °C and in extreme cases in excess of 300 °C.

Thermosets are stiffer and stronger than thermoplastics due to the molecular structure bound together by covalent bonds. However, differences are not dramatic; for polymer matrices typical moduli and strengths are 2–4 GPa and 50–100 MPa, respectively. In contrast, there is a significant difference in strain to failure; for thermosets it is usually 5% or less, but for thermoplastics it is generally greater than 50%.

While thermoplastic polymers clearly dominate as unreinforced plastics, thermosets heavily dominate in composite applications. The main reason for thermosets' domination is that they are more easily processed due to a viscosity one to three orders of magnitude less than melted thermoplastics. Moreover, for a comparable combination of mechanical properties and temperature tolerance, thermosets often have a cost advantage over thermoplastics.

The workhorse of thermoset matrices is unsaturated polyester, which offers an attractive combination of low price, reasonably good properties, and uncomplicated processing. Most unsaturated polyesters crosslink spontaneously at room temperature, following addition of a small amount of initiator, although moderate heating speeds up crosslinking.

Where mechanical properties and temperature tolerance of unsaturated polyesters no longer suffice, epoxies are often used. The improved properties of course come at a higher price and epoxies are therefore most often seen in fields where the cost tolerance is the highest, e.g., aerospace, defense, and sports applications. Most epoxies used in composite applications require an increased temperature to initiate the crosslinking and a well-controlled temperature history throughout the process to crosslink as intended. The crosslinking times of epoxies normally significantly exceed those of unsaturated polyesters.

Vinylesters are chemically closely related to both unsaturated polyesters and epoxies and in most respects represent a most successful compromise between the two. Vinylesters were developed in an attempt to combine the fast and simple crosslinking of unsaturated polyesters with the mechanical and thermal properties of epoxies. The fact that vinylesters are processed the same way as unsaturated polyesters is their major advantage.

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