

Chapter 6 Durability

6-1. Overview

a. FRP composites represent a new class of materials. Their durability is the primary reason for their use in many long-term applications of structural elements ranging from spacecraft to ladder rails, from aircraft wings to automobile doors, or from tennis rackets to liquid gas tanks. However, when a specific application is contemplated, it is essential for the designers to know not only the answers to questions regarding strength and stiffness, but also the question of how long the material will last under the conditions anticipated. These are the durability issues of a material.

b. In a general sense, the life of an engineering component is difficult to define. Many factors play roles in reducing the life. Most materials change characteristics by interaction with their surroundings over time. For example in the case of steel, oxidation leads to rusting. Presence of water accelerates the process. The exposure to sunlight makes nylon fiber turn yellow. Rubber ages faster and becomes brittle under the effect of ozone. Loss of water leads wood to split, and concrete degrades in harsh environment. What changes are likely to happen to FRP composites under given service conditions? If these changes are known beforehand, those changes can be accommodated in the design. And to accommodate these changes in the design, the rate of change and the effects of those changes on the behavior must also be known.

c. It is also important at the outset to define what is the limit of life; that means one must determine when the effective function of the structure ceases to exist following the period of service. For example, some materials, including polymeric composite materials, may not fail or separate under a certain service load condition, but can continue to deform or deflect beyond an acceptable limit. Thus, under these conditions the effective life ceases when a predetermined deformation or deflection limit is exceeded.

d. The mechanisms which control the durability of composites are well known. They include: (1) chemical or physical changes of the polymer matrix, (2) loss of adhesion or debonding at the fiber/matrix interface, and (3) reduction of fiber strength and modulus. Environment plays a crucial role in changing the properties of polymer matrix composites. By environment we mean here both the ambient environment and the loading environment

because both can affect the durability of the composites. Considering the ambient environment we find that both matrix and fibers may be affected by moisture, temperature, sunlight (UV radiation), ozone, and presence of degrading chemicals such as salts or alkalis. Repeated excursions to very high and low temperatures (freeze-thaw cycling), too, may introduce some changes. Under mechanical loading environment, as in steel, repeated loading may introduce fatigue in composites. Sustained load over a period of time may cause the material to creep. In this chapter we will briefly summarize the effects of various service factors which may affect the durability of FRP composites.

e. It is, however, important to note that because of the relative newness of these materials there is a considerable gap in the definitive durability data of polymeric composites. Systematic investigations to predict the life of most commonly acceptable fiber composites in civil engineering construction environments are rare and in many cases the data available are not relevant to practical applications.

6-2. Physical Aging of Polymer Matrix

One of the important aspects to consider in the durability issues of composites is the role of the polymer matrix and its change. The primary role of the matrix in the composites is for it to transfer stresses between the fibers, to provide a barrier against an adverse environment, and to protect the surface of the fibers from mechanical abrasion. Although its role in tensile load-carrying capacity is minor, it has a major influence on the inter-laminar and in-plane shear load transfer. Therefore, it must be of concern and importance if the polymer matrix itself changes its characteristics with time. It is normal for all polymers to undergo an extremely slow change of chemical (molecular) structure. The environment, mainly the temperature and humidity, controls this change. The process is known as aging. The reason is that when a polymer is cooled below its glass transition temperature, the material does not achieve instantaneous thermodynamic equilibrium. Instead, its free volume equilibrium evolves over time, and during this time the mechanical properties can change (Monaghan and Brinson 1994). However, it is important to note that different groups of polymers or even different molecular configurations within the same group of polymers would respond differently to the same environment. The aging effects are less severe in the most commonly available thermoset composites than in thermoplastic composites. As a result of physical aging some polymers can become stiffer and brittle, and thus can influence the matrix-dominated properties, namely the

shear and transverse response. But in most cases these effects are not critical because ultimately the major load-transfer process occurs through fibers, and the effects of aging on the fibers are minimal. While physical changes caused by aging are totally reversible once the polymeric material is heated above its glass transition temperature, this will typically not impact civil engineering structures since they will never reach the glass transition temperature.

6-3. Influence of Moisture

When exposed to humid air or water environments, many polymer matrix composites absorb moisture by instantaneous surface absorption and diffusion. Usually the moisture concentration increases initially with time and finally approaches the saturation point (equilibrium) after several days of exposure to humid atmosphere. The time to reach the saturation point depends on the thickness of the composite and the ambient temperature. Drying can reverse the process but may not result in complete attainment of original properties. The uptake of water by polymer composites in general follows the generalized Fick's law of diffusion. Figure 6-1 shows the typical Fickian behavior of a carbon-reinforced epoxy resin. In reality, however, the exact rate of moisture uptake depends on several factors including void content, fiber type, resin type, fiber orientation/architecture, temperature, applied stress level, presence of microcracks, and thermal spikes.

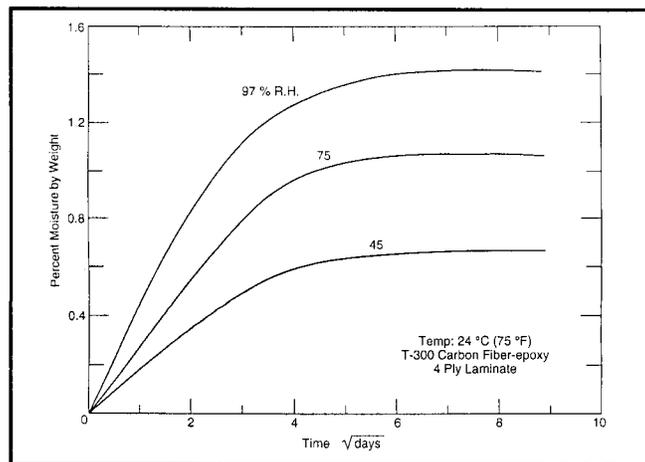


Figure 6-1. Water absorption behavior of polymer composites

a. *Influence of moisture on polymer matrix.* Absorption of water by resin in some instances may change the resin properties including the glass transition temperature through hydrogen bonding for the water molecules.

However, this is not of major concern in civil engineering applications of composites. It is only above the temperature level of 120 °C (248 °F) that the stiffness of the composite may drastically degrade if the glass transition temperature becomes lower from moisture absorption. Moisture absorption has one beneficial effect on composites: it causes swelling of the resin. The swelling of the resin matrix in the composite around the fiber reduces the residual compressive stresses at the fiber/matrix interface caused by the curing shrinkage. This results in release of the mechanical interlocking stresses between the fiber and the matrix which in turn can have increased load-carrying capacity. Hahn and Kim (1978) reported that in improperly manufactured composites where voids are present at the fiber/matrix interfaces or in the layers of composites, the ingress of water through the voids or interfaces can cause plastification of the resin. The water trapped in voids may result in blisters. However, the problems can be eliminated by judicious selection of resin materials, appropriate surface treatment of reinforcing fibers, and manufacturing techniques.

b. *Influence of moisture on fibers.* It is commonly believed that glass fibers can be damaged by prolonged exposure to water. The reasons are that glasses are made of silica in which oxides of alkaline metals are dispersed. The alkaline metallic oxides are both hygroscopic and hydrolyzable. However, the most common form of glass fibers for civil engineering composite applications are made of E- and S- glass, which contain only small amounts of alkaline-metal oxides, and so are resistant to damage by water. Nevertheless, the composites of glass fibers should be well fabricated to avoid any large-scale water ingress, because presence of water at the glass-fiber interface lowers its surface energy which in turn can promote crack growth. In addition, degradation over long periods of time and at high temperatures has not been studied. Aramid fibers can absorb considerable quantities of water resulting in swelling. However, most fibers are protected by coating (sizing) which ensures good bonding with the matrix and also serves to protect it from water absorption. Moisture does not have any known degrading effects on carbon fibers (Mallick 1988).

c. *General behavior of water-saturated composites.*

(1) The water-saturated composites usually display a somewhat increased ductility due to a softening of the matrix. This could be a beneficial aspect of water absorption in polymer composites and could possibly be used in limited cases. Limited degradation of strength and modulus can also occur in water-saturated composites. These degradation changes are mostly reversible, so that upon

drying the composite may regain most of its lost properties.

(2) It is also interesting to note that increase of hydrostatic pressure (for example, where composites are used in underwater or sea-bed applications) does not necessarily increase the water uptake and hence does not contribute to composite degradation. Thus, most underwater polymeric structures are expected to have high durability. In fact, under the hydrostatic pressure the water uptake is reduced slightly because of consequent closing of microcracks (microvoids) and interfacial defects (Burnsell 1989). However, recent research by the Naval Surface Warfare Center indicates that a significant increase in moisture may occur in some types of composites by hydrostatic pressure.

(3) Water absorption affects the dielectric properties of the composites. Presence of free water-filled microcracks can decrease this property dramatically.

6-4. Hygrothermal Effects

Temperature plays a crucial role in the water absorption mechanism of composites and its subsequent irreversible effects. Temperature influences distribution of the water, the quantity, and the rate at which it is absorbed. As the temperature increases, the amount and rate increase rapidly, as shown by Dewimille and Burnsell (1983). They have shown that damages induced by immersion in boiling water for only a few hours produced debonding and cracking of the same degree as at 50 °C (122 °F) over a period of 200 days. At room temperature the same composite specimens showed no indication of damage. These observations led to the development of a technique for accelerated aging tests of composites.

6-5. Alkaline Environment

In using glass fiber composites in alkaline environment it is essential to ensure that high-alkali-resistant glass is used, because the alkaline solution reacts with glass fibers to form expansive silica gels. This precaution is especially important for application of glass-fiber-reinforced composite material as reinforcing bars in concrete. Glass-fiber-reinforced polyester bars are being increasingly considered to replace steel-reinforcing bars in pavements which are corroded by deicing road salt. However, during hydration of the concrete, a highly alkaline (i.e., pH > 12) pore water solution is created. This highly alkaline solution can affect the glass fiber and reduce durability of the bars. Relatively inexpensive E-glass fibers are considered not to have much resistance against the alkali attack. Use

of vinyl ester resin has been observed to reduce the alkali attack by providing an effective barrier. The resistance to alkali attack can also be improved by designing the member to lower stress levels. High-alkali-resistant glass can improve the durability. There is continuing research regarding improving the long-term effects of alkaline environment on glass fibers embedded in polymer matrix. Results of the research, hopefully, will improve the FRP composite's durability in alkaline environment. It must be noted also that carbon and aramid fiber composites are not susceptible to alkaline environment degradation.

6-6. Low Temperature Effects

a. Extreme changes in temperature of composite materials result in several important effects. Most materials expand when temperature rises. In fiber-reinforced polymer matrix composites, the coefficient of thermal expansion of the matrix is usually an order of magnitude greater than that of the fibers. A decrease in temperature, due either to cooling during the fabrication process or to low-temperature operating conditions, will cause the matrix to shrink. Contraction of the matrix is resisted by relatively stiff fibers through fiber/matrix interface bonding, setting up residual stresses within the material microstructure. The magnitude of the residual stresses is proportional to the difference in curing and operating temperatures of the composite material. Except for a very severely cold environment the induced residual stresses are not of much concern. Where large temperature differentials exist (for example, in the Arctic and the Antarctic regions of the world), sufficiently large stresses may induce microcracking in the material. These microcracks in turn can reduce the stiffness of the composite, increase permeability and water ingress through fiber/matrix interface, and thus finally contribute to the degradation processes.

b. Another very important effect of lower temperatures is the accompanying change in matrix strength and stiffness. Most resin matrix materials become stiffer and stronger as they are cooled. These changes can influence the modes of failure. For example, Figure 6-2 shows the results of 1.5-in. (38-mm) diameter cylindrical specimens tested in compression at room temperature and at -50 °C (-58 °F). At the low temperature the compressive strength increased by 17.6 percent, but the material failed more violently (Dutta 1994). The energy absorption before failure at low temperature is higher than at room temperature. This particular aspect of high energy release at failure should be considered in designing with composites where impact loadings are expected at lower temperatures.

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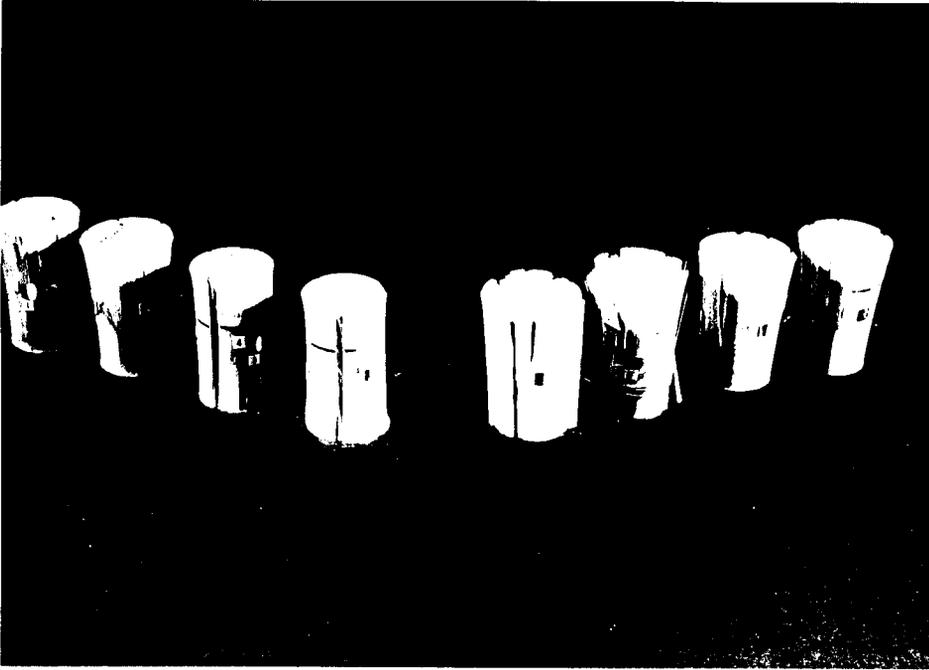


Figure 6-2. Composites failures are more violent at low temperature (right) than at room temperature (left)

6-7. Low Temperature Thermal Cycling (Freeze-Thaw) Effects

a. Unless a composite contains a significant percentage of interconnected voids that are filled with water, the freeze-thaw effects on the strength, within the normal temperature range (+30 °C to -20 °C) (+86 °F to -4 °F), are insignificant. Commercially available glass fiber composites usually contain about 0.4 percent voids, which does not allow any appreciable frozen moisture to cause any serious damage.

b. However, low temperature thermal cycling has other effects on composites. Residual stresses occur in composite materials due to differences in coefficients of thermal expansion of constituent elements in the material microstructure. Under extreme low temperature conditions these stresses can result in the formation of microcracks in the resin matrix or in the resin-fiber interface. The chances of microcrack growth under normal range of service temperatures, say between +30 °C and -20 °C (+86 °F and -4 °F), are usually remote or marginal. However, under severe thermal cycling conditions, for example, between +60 °C and -60 °C (+140 °F and -76 °F), microcracks can grow and coalesce to form matrix cracks which may propagate in the matrix or wander around the matrix-fiber interfaces (Lord and Dutta 1988). Under prolonged thermal cycling they continue to grow in

number and size and can result in stiffness degradation and degradation of other matrix-dominated properties.

c. The limited number of tests conducted at low temperatures (down to -50 °C) on composites at the Cold Regions Research and Engineering Laboratory (CRREL) of the Corps of Engineers have uncovered some basic problems of designing with composites for safety and durability at extremely cold environment (Dutta 1992). It has been observed that at very low temperatures the unidirectional tensile strength of all polymeric composites tends to decrease, although the off-axis and transverse tensile strengths increase. These results are explained by hardening of the polymeric matrix at lower temperatures. Prolonged thermal cycling between extreme temperatures has also shown degradation of off-axis strength and stiffness. These characteristic changes are important for structural design in cold regions.

6-8. Influence of Ultraviolet (UV) Radiation

The effect of ultraviolet light on polymeric compounds is well known. On prolonged exposure to sunlight the matrix may harden and discolor. The problem is generally overcome by applying a UV-resistant coating to the composites. Of major concern is the degradation of reinforcing polymeric fiber such as aramid. An example strength loss of 50 percent is reported for aramid fabric of

light weight, 75 g/m² (0.25 oz/ft²), after five weeks exposure in Florida sunshine (Larsson 1988). However, the effect is a self-screening type--that means only the skin of the composite structure is affected. So, in thicker composites the degradation effect is minimal on structural properties. For applications where surface properties are important, consideration should be given to reduce surface cracking due to sun rays.

6-9. Creep Behavior

a. Creep is the increase in strain with time at a constant stress level. Creep occurs because of the combination of elastic deformation and viscous flow. When the stress is removed after a period of time, the elastic deformation is immediately recovered, but the deformation caused by the viscous flow recovers slowly to an asymptotic value, called the recovery strain (Figure 6-3).

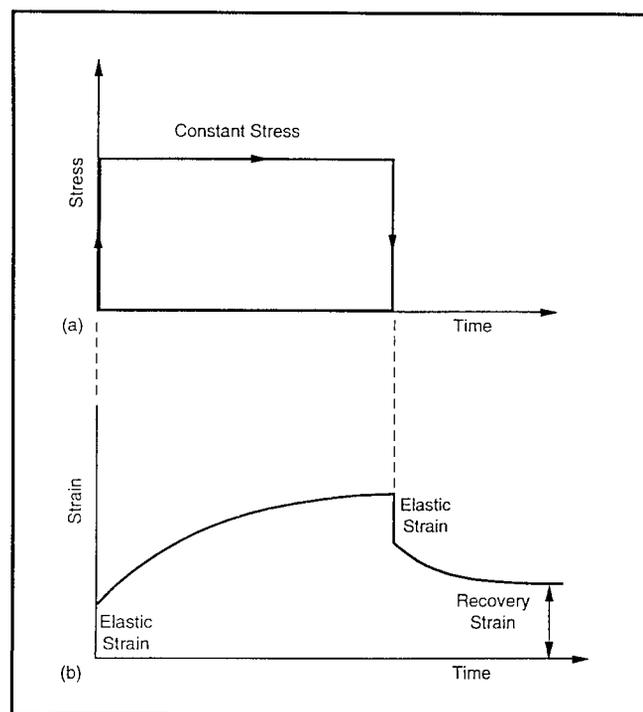


Figure 6-3. Schematic of the creep behavior of polymer composites

b. In composites, the creep strain depends on the stress level and temperature and is a function of both distribution of stress between the fiber and matrix. In general, highly cross-linked thermosetting polymers

exhibit lower creep rates than thermoplastic polymer composites. With the exception of aramid fibers, commercial reinforcing fibers such as glass and carbon do not creep appreciably at normal loads.

c. Creep data for composites can be generated by conducting a tensile or flexural creep test over a period of a few hours, and from these data the long-term creep behavior can be predicted by the time-temperature superposition method.

d. The modulus of a polymer (E) at time t and temperature T_o can be related to its modulus at time t_1 and temperature T_1 by the following equation (Mallick 1988).

$$E(t,T) = (\rho_1 T_1 / \rho_o T_o) E(t_1, T_1) \quad (6-1)$$

where ρ_1 and ρ_o are the densities of the polymer at absolute temperatures T_1 and T_o , respectively.

e. Figure 6-4 shows the tensile creep curves for a composite at various stress levels. For fiber orientation $\theta = 0^\circ$ creep is nearly constant, indicating that creep in the longitudinal direction of 0° composites is negligible. However, at other fiber orientation angles creep strain can be significant. Thus, it is important in polymer composite designs to recognize the influence of creep when the stresses are significantly large off-axis to fiber orientation.

f. Over a prolonged period of time a sustained load can induce a complete failure in a creep-prone material. The time at which the failure occurs is termed the "lifetime" or "stress rupture time." For a given composite material, stress rupture tests are usually performed to determine a range of applied stresses and lifetimes within which the material can be considered "safe" in long-term static load applications. The relationship between the applied stress level and lifetime is often represented as

$$\sigma_u = A - B \log t \quad (6-2)$$

where σ_u is the static tensile strength, and A and B are empirical constants.

g. Glass and aramid fibers over a long period of time exhibit failure by stress rupture. Carbon fibers are relatively less prone to stress rupture. Glaster and co-workers (1983, 1984) have generated extensive stress rupture data for S-glass and aramid composites.

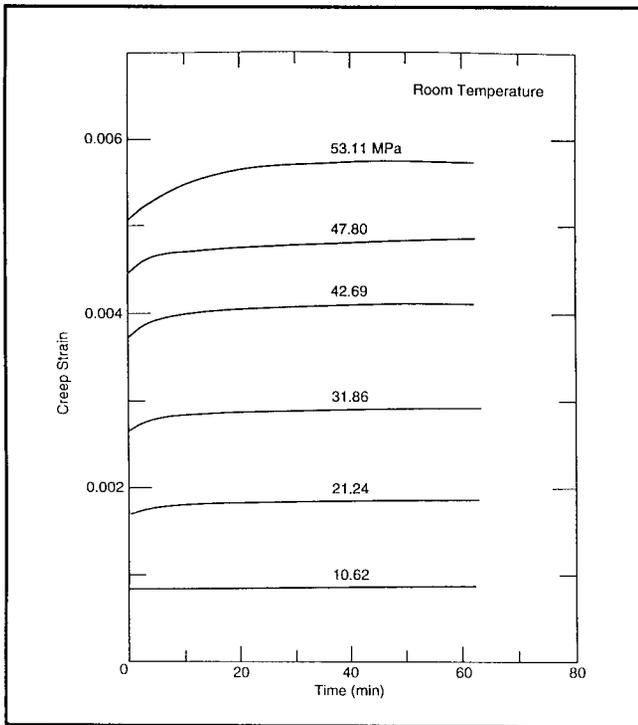


Figure 6-4. Tensile creep curves for a vinyl-ester/glass composite at various stress levels (after Mallick 1988)

6-10. Fatigue Properties

a. The fatigue properties of a structural material represent its response to cyclic loading. Repeated cyclic loading usually results in a decrease in the strength properties of metallic materials. Composites, on the other hand, generally are considered to have excellent fatigue response.

b. The fatigue behavior of a material is usually characterized by an $S-N$ diagram representing the relationship between the stress amplitude (S) and the number of cycles (N) to failure on a semilogarithmic scale (refer to Figure 6-5). In general, the number of cycles to failure increases continually as the stress level is reduced. For mild steel, a fatigue limit is of the order of 10^5 - 10^6 cycles at 50 percent of its ultimate tensile strength. Below the fatigue limit, the likelihood of fatigue failure occurring is very low, so that the material has essentially an infinite life.

c. One of the major problems of predicting fatigue failure limit of composites is the complexity in assessing the modes of failure. The most commonly used fatigue test on composite materials is the tension-tension cycling.

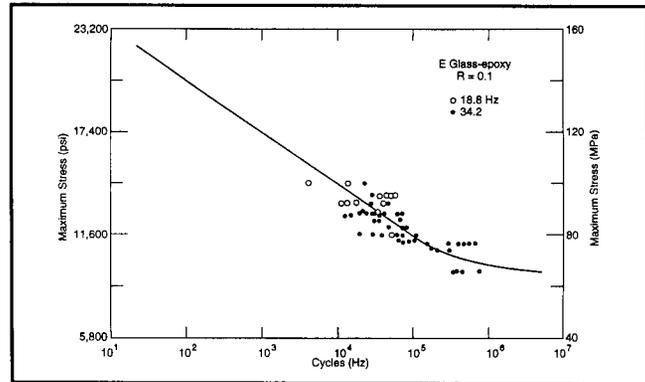


Figure 6-5. A typical fatigue behavior of an E-glass-epoxy composite

Tension-compression cycling by flexural fatigue tests are also being reported. The tension-tension fatigue cycling test procedure is described in ASTM D 3479.

d. The compression-compression fatigue performance of composites is generally less satisfactory than the tension-tension performance. In flexural fatigue loading, therefore, the initial damage usually develops on the compressive side of the specimen.

e. A unique feature of a fiber composite material in fatigue testing is that it exhibits a gradual softening with increased cycling. Thus, tests are sometimes done not to a failure represented by the separation of the specimen, but to a limit of specimen stiffness or residual strength which is predetermined.

f. The $S-N$ curve for the fiber composites can be represented by a straight-line relationship given by

$$S = \sigma_u (m \log N + b) \quad (6-3)$$

where

S = maximum fatigue stress

σ_u = static strength

m, b = constants

N = number of cycles to failure

Values of m and b for E-glass/epoxy 0-degree fiber orientation are 0.1573 and 1.3743, respectively (Lorenzo and Hahn 1986).

g. It has generally been observed that in tension-tension fatigue tests the unidirectional carbon and aramid composites exhibit exceptionally good fatigue strength. On the other hand, when the fibers are oriented in off-axis directions the fatigue strengths often depend on the proportion of fibers aligned with the loading axis, stacking sequence, and parameters of cycling. It should be noted that a tension-compression cycling may produce a steeper *S-N* plot than the tension-tension cycling. The fatigue performances of both E- and S-glass fiber-reinforced composites are poorer than those of carbon or aramid composites. Results of a tension-tension fatigue test for a 0-degree E-glass-epoxy laminate are shown in Figure 6-5.

6-11. Fire Hazards and Flammability

a. FRP composites used for any structural construction must comply with the local construction code requirements including fire resistive and other life-safety specifications. At present the coverage of structural composites in building or other construction codes is not extensive. It is, therefore, imperative for designers to work closely with the building or construction authorities early in the selection process to establish the fire-resistive requirements of the selected composites which may have to be verified by fire tests. Where fire hazard exists, the fire-hazard characteristics (including the intended use of the structure to be designed, potential ignition sources,

potential mode of flame and smoke spread, and means for detection, suppression, and extinguishment) must be identified and the proper building code and other fire code requirements determined. The specific standards for plastics in a model building code have been summarized by Heger (1981). The following is a typical example:

The approved plastic materials shall be those that have self ignition temperature of 650 °F or greater when tested in accordance with the Uniform Building Code (U.B.C.) Standard 52-3 (ASTM D 1929) and a smoke density rating not greater than 450 (ASTM E 84). Approved plastic shall be classified in accordance with U.B.C. Standard 52-4 (ASTM E 84).

b. Fire tests for FRP composites are to be based on end use, quantity, location, and special requirements by the owner. After identifying the fire hazard, a suitable test method must either be selected from standard tests or developed for the specific need. These include ignition tests, flame spread tests, extinguishment, smoke evaluation, and tests for toxicity and fire endurance. Table 6-1 summarizes some of the standard fire tests. A review of industry literature on FRP composites shows that flammability properties are usually specified by the manufacturers. Typical values recorded by some manufacturers are given in Table 6-2.

Table 6-1
Fire Tests of Building Materials

Test Type	Test Methods	Object
Ignition tests	ASTM D 1929	Measures flash-ignition temperature
	ASTM E 136	Material is classified as combustible or not
Flame spread tests	ASTM E 84 (Tunnel test)	Measures surface flame spread, smoke generation, and total heat release
	ASTM D 635	Measures horizontal burning rate
	UL-94	Measures inflammability in vertical bar specimens
Tests for smoke evaluation	NFPA 258	Measures maximum optical smoke density
Tests for fire endurance	ASTM E 119	Determines flame penetration on unexposed face and structural collapse

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Table 6-2
Typical Inflammability Properties Reported in Industry Literature

Fire and Flammability Properties	Test Method	Material ¹	Value
Flammability classification	UL 94 V-O	Extren 525 and 625 Pultrex 1525	Pass
Tunnel test	ASTM E 84	Extren 525 and 625 Pultrex 1525	25 Max 25
NBS smoke chamber	ASTM E 662	Extren 525 and 625	650-700
Flammability	ASTM D 635	Extren 525 and 625 Pultrex 1525	Self-extinguishing No ignition

¹ Names used were obtained from industry literature for the purpose of identification only. See references of these in Appendix A.