

ENVIRONMENTAL EFFECTS

Composite materials and structures experience two distinct external environmental conditions

- (i) ground (and near ground) environment and
- (ii) space environment.

The former is primarily dominated by the temperature and the humidity. The presence of oxygen, sodium chloride, sulphuric acid and certain other aggressive chemicals in the lower atmosphere is also of major concern. All ground-based materials and structures including aircraft and other flight vehicle structural components are likely to be affected by ground environments during their service, manufacturing and storage. The damage due to foreign body impact is also to be viewed with all seriousness, as it may lead to abort a mission or call for a major repair. The impact damage may occur owing to accidental dropping of a hard object (tool, nut, bolt, etc.) from a height. Aircraft are also quite often hit by birds (soft objects) while flying through hailstone forming clouds. The engine fans, compressor blades or the aircraft body is normally affected by such impact. The major environmental problems that are encountered by space vehicles during their flight and orbit in space are due to radiation, thermo-vacuum environment and meteoroid impact. In the present chapter we discuss some of these problems involving both ground and space environments and their effects on composite materials and structures.

GROUND ENVIRONMENT

Corrosion

Corrosion of a composite material involves the chemical or physical deterioration of its constituents (including the fibre matrix interface and the protective surface coat) when exposed to a hostile environment. Chemical degradation means weakening and/or breakage of chemical bond due to reaction of constituents with each other or the corrosive medium. The process of chemical degradation is irreversible. Physical deterioration involves only physical changes and the process is reversible. For example, the swelling of a polymer composite due to absorption of moisture is a physical degradation process, and the swelling is removed when the moisture is fully desorbed. Corrosive environments are essentially of two types: gaseous and aqueous. The potential reactants in the gaseous environments are O_2 , C , Cl_2 and S_4 which are abundant in the ground environment. Oxidation is the most commonly observed corrosive phenomenon in a gaseous environment. Almost all metal matrices form oxides with gaseous oxygen. The rise of temperature may accelerate the oxide nucleation process. The nucleation of the oxide

normally takes place at favourable sites on the metal oxygen interface. The formation of solid oxide scales may slow down the oxidation rate by preventing direct contact of the metal matrix with the oxygen. Liquid oxides usually flow off and volatile oxides vapourise and therefore offer little resistance to oxidation. Ceramic matrices, on the other hand possess excellent oxidation resistant properties. The oxides such as alumina, beryllia, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), silica, titanium oxide, nickel oxide, zirconia, hafnia, yttria and thorium oxide are more stable in air at high temperatures compared to other ceramics such as nitrides, carbides or sulphides. Carbon and glass fibres exhibit corrosion when subjected to CO and CO₂ vapours. Carbon fibres are more susceptible to oxidation in presence of oxygen. Oxidation occurs on the surface and in the cracks and cavities of the fibre. The rate of oxidation is dependent on the fibre texture, inclusions, porosity and surface condition. Glass fibres with higher silica content exhibit more resistance to corrosion. Thermoplastics, in general, possess excellent oxidation resistant properties. Oxidation of thermosets occur due to chain reactions of free radicals with oxygen that diffuses into the composite. Water is the most corrosive electrolyte that causes all common types of corrosion. The dissolved oxygen in aqueous solution is the major driving force to initiate corrosion at crevices that are formed by settlement of sand, debris and marine growths on the composite surfaces or that exist in joints and other flaw sites. Graphite fibre reinforced aluminium matrix (AA6061) composites exhibit accelerated corrosion when both graphite and aluminium are exposed to saline environment due to pitting, crevice corrosion or erosion of the protective aluminium surface layer. The formation of aluminium carbides at the fibre-matrix interface alters the properties of the aluminium bond layer in the affected regions and accelerates the corrosion process. A couple of general observations can be made based on similar studies of several metal matrix composites:

1. Most fibres and matrices corrode when exposed to a corrosive environment.
2. Erosion of protective layer and pitting accelerate the corrosion process.
3. The properties of the reinforcement/matrix interface may control the corrosion nucleation process at favourable sites.
4. The existence of disbonds, fissures, elemental segregation, inhomogeneity, nonuniform plastic deformation, cold worked regions, residual stresses, etc., may influence the corrosion process.

An appropriate protective coating, in most cases, provides a barrier between the composite and the corrosive medium and slows down the corrosion rate. Sulphuric acid anodizing and organic coatings have been found to be effective for corrosion control of graphite filament reinforced aluminium composites, whereas electroplated or vapour deposited nickel

and titanium coatings may create highly unfavourable anodic (aluminium) and cathodic (nickel or titanium) area ratio at the coating flaw sites for corrosion acceleration. A surface coat of flame or arc sprayed aluminium (plus an organic top coat) may decelerate corrosion in silicon carbide/aluminium composites. One undesirable characteristic of glass fibres is that they are soluble with either very high or very low pH level. The corrosion of a glass fibre takes place when the negatively charged hydroxyl ions attack the positively charged silicon ions and the positively charged hydrogen ions attack the nonbridging negatively charged oxygen ions. Suitable surface treatment (sizing) is generally made to control such corrosion. Reinforced plastic boat hulls exhibit blistering (also known as boat pox, aquatic acne or plastic plague) at the outer surfaces. The blistering is caused due to osmotic effects. An osmotic pressure builds up due to the presence of a solute within the composite, when a solvent (water or dilute sodium chloride solution) diffuses through the thin gel coat (which acts as a semipermeable membrane) and causes formation of blisters.

Moisture Diffusion

All polymers absorb moisture in humid environment or when immersed in water. The measured critical surface tension of most polymers (18-50 dyn/cm) is lower compared to the surface tension of water (72.8 dyn/cm). All polymers are therefore hydrophobic. Diffusion is the process by which water is absorbed by a polymer. The extent of moisture absorption by a particular resin depends on the affinity of its polar functional groups for water molecules. The process of diffusion is distinctly different from the capillary action by which water is transported through fissures, cracks, voids, etc. In the case of moisture diffusion, water is not absorbed in the liquid form, but in the form of molecule or groups of molecules linked by hydrogen bond to the polymer. The absorption or desorption of moisture is governed primarily by the moisture gradients that arise due to non-uniform distribution of moisture. The transportation of mass takes place from the region of higher concentration to one of lower concentration. There are several other factors such as temperature, relative humidity, area of exposed surface, fibre and matrix diffusivities, resin content and fibre shapes that influence the moisture diffusion process.

Moisture absorption or desorption characteristics can be modelled using a simple one-dimensional form of Fick's diffusion equation

Where,

C is the moisture concentration (g/m^3),

d_{22} is the diffusivity (m^2/s) and

t is the time (s).

The Fick's relation defined in Equation is fundamentally equivalent to Fourier's heat conduction equation. The diffusion coefficient, d_{22} is a material constant and gives the measure of the rate at which moisture diffuses through the composite along the x_2 -axis.

The maximum moisture concentration within the composite reaches the level of C_0 so as to be equilibrium with the outside moisture concentration (i.e., C_0), when it is exposed for a long time. Hence the maximum moisture content is given by

$$M_m = C_0 / \rho$$

After a long exposure, the moisture content of the composite reaches asymptotically to the maximum moisture content, M_m . Note that the value of M_m is a material constant, when the composite is immersed in water. When the composite is exposed to humid environment, M_m varies with the relative humidity, f as given by

$$M_m = a^{\phi b}$$

Where the constants a and b (for a particular composite) are determined from the best fit curve for the M_m vs. ϕ plot. The diffusion coefficient d_{11} and d_{33} can also be determined in a similar manner. The moisture diffusion coefficient is normally dependent on temperature, T and can be expressed as

$$d = d_0 \exp(-A/T)$$

The spatial distribution of moisture concentration, at a time t can be obtained for particular boundary conditions solving the given equation using the finite element method or other numerical analysis techniques. The analytical solutions are however, available for simple one dimensional and a few two-dimensional problems. The finite element analysis technique, on the other hand, can be extended to tackle three-dimensional moisture diffusion problems and is a convenient means to solve hygrothermal (both moisture and temperature) diffusion in a composite body having complicated geometry with multidirectional fibre orientations and complex boundary conditions. The changes in the moisture concentration and temperature may introduce thermal stresses and strains in a laminate

Practical composites may exhibit non-Fickian diffusion behaviour. The anomalous Fickian diffusion behaviour is observed, if cracks, voids, delamination and fibre matrix interface debond exist in the composite and when the matrix itself exhibits non-Fickian behaviour. The existence of cracks, voids, etc., increases the moisture absorption at a faster rate. The non-Fickian behaviour of the polymer is observed when the relaxation processes inside the polymer progress at a rate comparable to the diffusion processes. The absorbed

moisture may decrease the temperature thereby affecting the diffusion process. Fick's law is generally applicable to rubbery polymers, but fails to characterize the diffusion process in glassy polymers. It is, in general, observed that there exists an upper limit of humidity or temperature at which moisture diffusion deviates from that governed by Fick's law. However, much more research effort is needed to understand and analyse the effects of non-Fickian diffusion in polymer composites.

Foreign Object Impact

The impact considered here, is defined as the phenomenon involving collision of two elastic bodies, in which the striking object (or the impactor) has relatively less mass compared to that of the target. Examples of such impact involving composite structures (i.e., targets) are too many. A few typical examples are a bird striking an aircraft engine blade, a hailstone impacting on the aircraft wing skin, a bullet hitting a composite vest or car body panel, or a ball bouncing off a composite hockey stick. The impacting velocity in these cases mostly range from Mach 1 down to a few metres per second. Such an impact phenomenon is normally termed as low velocity impact. The material behaviour of the striker and the target even in the highly stressed impacting region is assumed to follow the constitutive relations defined in the realm of solid mechanics.

Consider a simple case of an elastic spherical mass impacting at the mid-span of a unidirectional composite beam. The transverse vibrational response of the beam is then governed by the following relation:

$$D_{11}W_{1111} + P_w = F_c(t)$$

Where $F_c(t)$ is the time-dependent contact force exerted by the impacting mass at the contacting mid-span of the beam.

The impactor motion is governed by

$$M_i w_i + F_i(t) = 0$$

Where the subscript 'i' refers to the impactor.

The contact force $F_c(t)$ during loading can be determined by the modified Hertzian contact law as given by

$$F_c(t) = n \alpha^{3/2}$$

Where α is the local indentation on the target at the contact point and n is the modified Yang-

Sun contact stiffness. Note that the value of α is time dependent and it is the

difference between the impactor displacement, w_i and the target displacement, w at the contact point at a time t after the initial contact.

The typical value of α_{cr} for a carbon/epoxy composite is $8.0264 \times 10^{-5} \text{m}$.