

Strategies for stable composite structural design

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ABSTRACT

Advanced composites have been effectively used in space applications such as telescopes, optical benches, and metering structures. As the sophistication of optics and instrumentation increases, the need for near-zero outgassing and extremely dimensionally stable composites becomes of paramount importance. Continuing improvements in resin and reinforcing fiber technology have resulted in a wider selection of materials for the composite designer of dimensionally stable structures. Additional improvements in metal sealing techniques promise unprecedented long-term environmental stability. These new options allow the designer to develop a dimensional stability strategy which conforms to design requirements and yields an optimum, cost-effective composite design approach. This paper addresses the major stability issues in composites and how stability can be predicted for long-term applications, along with design options to achieve program goals. Low-moisture-absorbing composites based on cyanate esters, metal sealing techniques, and long-range stability are also addressed.

1. INTRODUCTION

Although composites have been utilized in dimensionally stable optical structures for over 15 years¹, various inherent dimensional instabilities exist with composites, including potential hygroscopic and thermal changes. Thermal changes can be minimized by the proper fiber volume and modulus selection in the composite design. Hygroscopic instabilities are harder to control since impermeable barriers must be applied to prevent dimensional changes from occurring. To protect the structure from dimensional changes caused by moisture, bonded metal foils or eutectic metal coatings are typically employed as moisture barriers². In protected laminates, metal barriers also offer the design option of tailoring the composite coefficient of thermal expansion to a near-zero level by adjusting the thickness of the coating. In addition to barriers, the reinforcing fiber modulus can be increased to minimize the response of the composite to moisture absorption. The matrix resin itself can also be modified³ to absorb minimal quantities of water. Since dimensional change is proportional to the amount of moisture absorbed, relatively small dimensional changes can be achieved. Recently developed moisture diffusion models^{4,5} have been shown to predict moisture ingress into metallized (but slightly flawed) barriers. This paper describes strategies which can minimize the effects of moisture diffusion into dimensionally stable composite structures. A multidimensional influence matrix has been developed which indicates the best methods for achievement of maximum dimensional stability in composites.

2. DISCUSSION

2.1. Factors which affect dimensional stability

Two types of dimensional stability are generally pursued for high modulus composites: thermal stability and moisture-induced stability. Thermal stability is achieved by the proper volumetric balance of a high-modulus, reinforcing fiber having a negative coefficient of thermal expansion (CTE), α , and a matrix resin with a positive CTE. The CTE is defined as the strain change per degree of temperature change (ppm/°F). A composite comprised of a 75 msi pitch fiber at 57-58 percent fiber volume in an epoxy matrix is typically employed to achieve a near-zero CTE (< 0.05 ppm/F). Moisture-induced expansion of a composite results when water diffuses into the matrix resin causing a volumetric matrix change. The coefficient of moisture expansion (CME), β , is defined as the strain change per percent of moisture absorbed.

Many factors affect the degree of dimensional change in a composite exposed to moisture. The major influences on the degree of hygroscopic strain in a composite are:

- Fiber modulus
- Fiber volume
- Temperature
- β coefficient
- Relative humidity
- Diffusion constant
- Equilibrium moisture content of the resin
- Time of exposure
- Laminate thickness

If the laminate is protected with a metal foil or eutectic, flaw areas also become important. The two largest influences on moisture-induced composite strain changes are the fiber modulus which provides a resistive force to the expansion of the matrix resin during moisture absorption and the quantity of moisture in the resin at saturation.

Figure 1 illustrates the effects of fiber modulus on the isotropic CTE, α , of a typical composite (calculated from the micromechanical equation in Reference 6). The degree of thermal expansion, α , is important when protective measures are taken with the composite. The more negative the α of the composite, the thicker the foil or eutectic coating can be to obtain a net near-zero CTE (Figure 2). As the protective coating thickness increases, the level of sealing generally increases. Figure 3 shows how the moisture expansion of a typical epoxy affects composites of various fiber moduli. As the in-plane modulus increases, the effect of moisture on strain change decreases. Note the large decrease in strain change when the matrix resin is changed to a cyanate ester resin to absorb less water than the typical epoxy matrix.

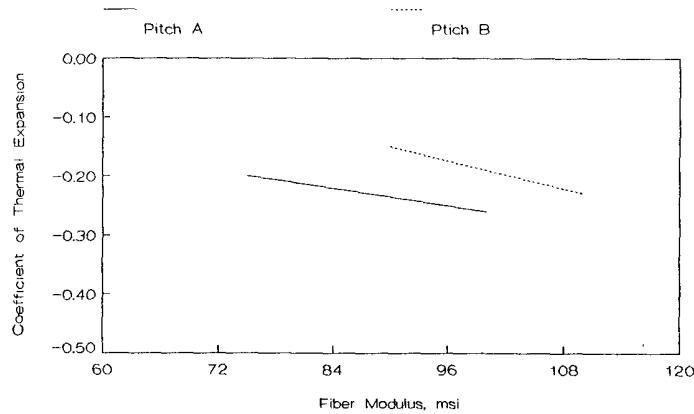


Figure 1. Calculated coefficient of thermal expansion of isotropic laminates versus fiber modulus

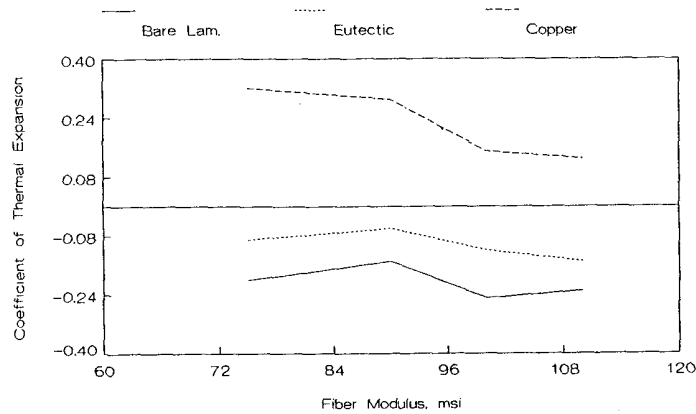


Figure 2. The effect of various 0.0025 cm-thick metal barriers on isotropic laminate coefficient of thermal expansion

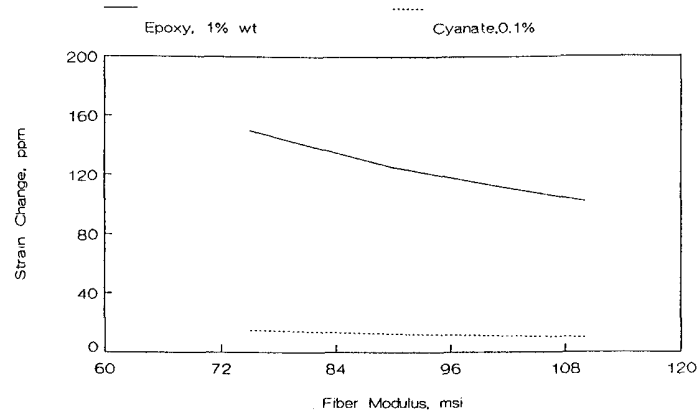


Figure 3. Moisture expansion of isotropic laminates versus fiber modulus

2.2. Moisture diffusion

A previous paper (Reference 4) has demonstrated the utility of employing Equation 1 to predict moisture levels in graphite/resin laminates. This model can be employed to predict moisture uptake/loss rates for metallized composites employed in dimensionally stable structures which contain a finite number of flaws:

$$M/M_{SAT} = 1 - (0.5)^{T^{1/2}} \quad (1)$$

where $T = D't/h$, D' = diffusion constant, t = real time, h = laminate thickness, and T = normalized time unit.

Flaws are defined as unsealed areas of the laminate and can be expressed as a fraction of the total surface area:

$$\text{Flaw Fraction, } F_s = A_F/A_T$$

where A_F = area of flaws in cm^2 and A_T = total area in cm^2 .

Since the expression for moisture diffusion contains D' (the diffusivity of the laminate), the flaw fraction term can be applied to adjust the expression (2) to (3):

$$M/M_{SAT} = 1 - (0.5)^{(D'.t./h)^{1/2}} \quad (2)$$

$$= 1 - (0.5)^{(D'.t.F_s/h)^{1/2}} \quad (3)$$

In effect, diffusion has only been allowed in these exposed cell fractions. The diffusion, in fact, is more complicated because adjacent cells (y and z directions) are empty and three-dimensional diffusion now occurs. The rate of ingress does not change, but the equilibrium point moves to the right on a given time scale. If a sealed laminate (1 percent flaw level) is compared with an unsealed laminate, the unsealed laminate gains moisture rather quickly and its rate of moisture uptake per time unit slows as it approaches saturation (80 percent). In a sealed laminate, the amount of moisture diffusion is quite small, but the rate appears to be linear until higher moisture contents are attained. The unsealed laminate gains moisture more quickly, although a much slower rate occurs as saturation is approached. The flawed sealed laminate moisture diffusion rate thus becomes competitive at longer exposure times. This means that over long periods of time, even low levels of flaws begin to play a significant role in dimensional stability.

The reverse situation is also interesting. If a sealed (but slightly flawed) structure is sent into space and begins to outgas based on its flaw density (F^s), it takes an extremely long period of time to lose this small amount of water.

Figure 4 illustrates the mathematical model of moisture absorption (Equation 1) into composite material. The x-axis is in a normalized time unit, T , and the y-axis is in the fraction of moisture absorbed under specific environmental conditions (M/M_{SAT}). Note that 50 percent of the moisture absorption occurs within the first time unit. Since $T = D \cdot t/h^2$, where D is a diffusion constant, t is the real time and h is the laminate thickness, and h is generally small for lightweight space structures, a rather rapid increase in weight or moisture fraction occurs. Table 1 shows some typical diffusion constants obtained for epoxies and cyanate resins, as well as the time required to absorb 50 percent equilibrium moisture at 0.10 cm thickness.

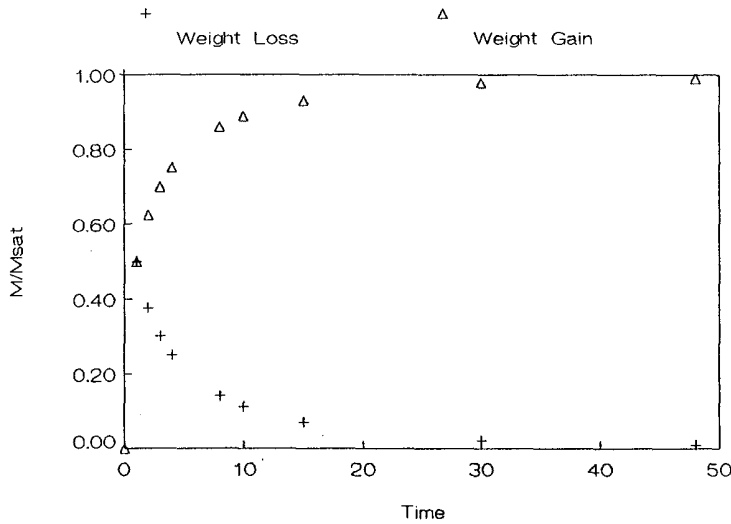


Figure 4. Mathematical model of moisture absorption/desorption (Equation 1)

Fiberite 954-3

Relative Humidity	<u>35%</u>	<u>55%</u>	<u>75%</u>
D'	0.0503	0.0569	0.0569
M_{sat} , %	0.152	0.185	0.236

Narmco 5208

Relative Humidity	<u>45%</u>	<u>75%</u>
25C D'	0.0363	0.0241
45C D'	0.0114	0.0965

Amoco 1939-3

Relative Humidity	<u>50%</u>
D'	0.0312
M_{sat}	0.235

Table 1. Diffusion constants (D' , cm/day) of various resin systems

Metallic coatings can slow the diffusion process considerably depending on the flaw level in the coating. At a 1 percent flaw level, significant amounts of moisture can diffuse into the laminate. Figure 5 illustrates the moisture diffusion into sealed composites with a 1 and a 0.01 percent flaw level as derived from Equation 1.

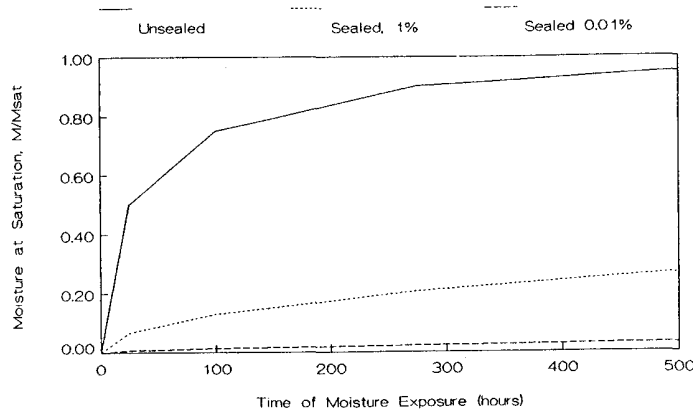


Figure 5. Sealed laminate moisture diffusion rates

In practical applications, a total seal of the composite is difficult to obtain. Therefore, to minimize the effect of the absorbed moisture, a material/process strategy must be developed to control the problem. The most obvious approach is to utilize a high-modulus fiber and a low moisture absorbing resin system, such as a cyanate ester. The strain changes in the composite are now potentially 10-15 ppm, at saturation at nominal relative humidity conditions. If a metal coating is added, two changes occur:

1. the CTE becomes more positive and is dependent on the thickness, modulus and α of the applied metal and,
2. the rate of moisture absorption decreases.

The moisture diffusion model in Figure 4 shows that 50 percent of the moisture (and approximately the total strain) occurs rather quickly on the unprotected composite. If the composite is assumed to already contain moisture to a 50 percent level, the absorption time to gain the other 50 percent is quite long. Conversely, moisture loss in space at a 50 percent level occurs very slowly compared to a near-saturated composite. The application of a barrier further slows the rates, making strain change over long time periods almost insignificant if the flaw levels are maintained to a 0.01 percent level. Figure 5 illustrates the moisture absorption which occurs in an epoxy composite at various flaw levels of a protective barrier. Equation 1 can be modified to reflect the effect of flaws in the barrier (Equation 2) and predict the subsequent strain changes when exposed to moisture.

The flaw level of a moisture barrier can be measured by weighing sample coupons over time to a specific moisture exposure. At 30 percent resin content, a typical cyanate will absorb 0.1 percent moisture or 3.0 mg for a 10 g specimen. When Equation 3 is used to calculate the time necessary to detect a 0.1 or 0.2 mg change in weight, a 0.01 percent flaw level is shown to require approximately 1,000 days.

For this time determination, the sample is assumed to be completely dry before the test. Epoxy resins which absorb much higher quantities of water would be measurable much sooner. Obviously we cannot wait 1,000 days to detect low flaw levels so alternate methods of detection are necessary (e.g., mass spectrometer techniques, microbalances).

3. OPTIMUM DIMENSIONAL STABILITY STRATEGIES

Several design routes are available to achieve maximum dimensional stability of composite structures. The following options are listed in decreasing order of stability.

3.1. Option 1 -- Maximum dimensional stability (<1 ppm strain change)

The highest stability would be achieved if the laminate contains a relatively high modulus fiber, a low moisture absorbing resin (such as a cyanate ester), which is partially saturated with moisture, and a metal seal with a low flow density (0.1-0.01 percent). The metal barrier thickness is such that the net CTE is 0.00 ± 0.05 ppm/°F. Diffusion rates in structures designed with this option would be so low to essentially have no effect on the dimensions over a several-year-storage window.

3.2. Option 2 -- Excellent dimensional stability (1-2 ppm strain change)

A melt-applied eutectic on a composite requires the composite to be very dry so that flaws do not occur during application of the eutectic through vaporization of its moisture at high temperatures. This option has been demonstrated to be almost two orders of magnitude better than a "normally applied" eutectic when care is taken to rigorously dry the laminate prior to sealing. Option 2 requires a near-zero CTE laminate since the eutectic modulus is not high enough to drive a more negative CTE to zero unless rather thick coatings are employed (2-4 mils). Since weight is always a prime consideration in space structures, the thinnest, most functional barrier is desired.

3.3. Option 3 -- Moderate dimensional stability (3-5 ppm)

High modulus fibers, a low moisture absorbing resin but a rather flawed (1.0 percent) barrier, a composite with predicted strain changes of $\pm 3-5$ ppm can be produced. Storage conditions and time must be controlled somewhat.

3.4. Option 4 -- Moderate dimensional stability (5-10 ppm)

Although the strain change due to moisture is 5-10 ppm, the CTE is more negative than typically desired. In controlled environments (i.e., where the ΔT is minimal), this approach may be cost effective. This approach employs only a high-modulus fiber and a low-moisture-absorbing resin system. If the relative humidity in storage is controlled (<50 percent relative humidity), reasonably good dimensional stability can be achieved.

4. EXPERIMENT RESULTS

4.1. Option 1

Quasi-isotropic coupons were prepared from 90 msi pitch fiber (K135) in a cyanate ester resin matrix (Fiberite 954-3). The coupons were rigorously dried to constant weight and allowed to absorb approximately 50 percent of the theoretical saturation quantity of moisture (M_{SAT}). The coupons were then metallized to effect a moisture seal on the material. The weight of the coupon after sealing indicated a barrier thickness of approximately 0.0015 cm.

Exposure of the coupons for over three months has produced no weight or dimension change. Pitch P75 and 954-3 specimens were also sealed in this manner and have been exposed for over 9 months with no moisture uptake. The CTEs of these specimens are more positive due to the higher CTE and modulus of the metal seal.

4.2 Option 2

Pitch 75S and ERL1962 coupons were dried in an oven at 100°C for 7 days under vacuum. The temperature was then increased to 150°C for 24 hours. The dried specimen was then eutectic coated per our standard process (COPS-0007) and submitted to TRW for testing of outgassing. The specimen was compared to a "standard" coupon which was not dried as rigorously. Although the dried specimen outgassed, its level of mass loss was about 80 times less than the standard coupon, making its flow level approximately 0.03 percent.

4.3 Option 3

Figure 6 illustrates this sealing option compared to an unsealed specimen and the dimensional stability it provides. This option is COI's standard method of sealing composites.

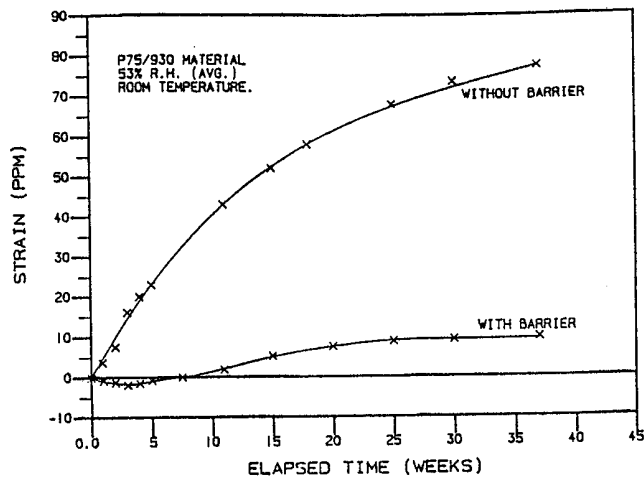


Figure 6. Exposure of bare and deposited metal-coated (moisture barrier) specimens to humidity

4.4 Option 4

Figure 7 illustrates the strain change for P75S/954-3 coupons after exposure to a 65 ± 5 percent relative humidity environment to saturation. Even lower values than an average of 9 ppm can be achieved if better storage conditions are employed.

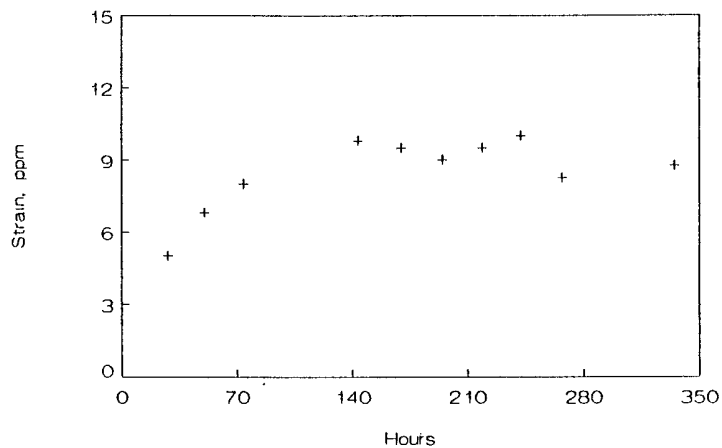


Figure 7. Moisture strain for isotropic P75S/954-3 coupons at 65 percent relative humidity

5. RECOMMENDATIONS AND CONCLUSIONS

The stability of composites in both thermal and hygroscopic environments can be quite high if proper design strategies are employed to prevent these effects. The degree of stability is dictated by the system requirements. New fibers and resin systems can be employed for minimal environmental effects. New material databases are required for design efforts and special quality assurance measures taken to ensure minimum levels of environmental performance.

Since some of the techniques involve complete metal sealing of detail parts, investigations of assembly techniques such as bonding or soldering are recommended. The metal-to-composite interface is not as strong as the typical interlaminar properties of a composite. New designs may be necessary to minimize the loads on these materials.

6. ACKNOWLEDGMENTS

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