Moisture Induced Dimensional Changes in Composites

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SUMMARY: All organic matrix composites absorb moisture and low molecular weight molecules, causing changes in dimensions and most other thermal and mechanical properties. With continued research a wide variety of moisture induced behavior is becoming recognized, such as non-Fickian diffusion, relaxation, and hygro-thermal-mechanical coupling effects. New techniques are required to adequately measure and quantify these behaviors. This paper describes a much needed advance in simultaneous and non-contact measurement of sample temperature, weight change and strain under controlled environmental conditions. Results are presented for conventional and accelerated methods of determining the coefficient of moisture expansion. Results are also presented on the CME determined by short term simultaneous strain and weight change. Extension of these techniques to studies of hygrothermoelasticity and fiber behavior are discussed.

Keywords: Moisture expansion, composite laminates, absorption, techniques

INTRODUCTION

Coefficients of thermal expansion (CTE) and moisture expansion (CME) are common design parameters for polymeric matrix based fiber reinforced composites. These are by definition equilibrium properties but since their use and measurement involves heat, mass transfer and a variable stress state there is the possibility of simultaneous cross coupling in their response and the possibility of material property changes as a result. The disparity between thermal and mass diffusion rates also assures that time is an important variable in the determination of moisture induced dimensional changes in polymer based materials and composites.

In this paper we address several topics related to the measurement and use of CME data. We start with a review of current methods of CME measurement and indicate a new approach which we call accelerated CME testing. A brief review of the subject of hygrothermoelasticity outlines areas where additional (cross-coupling) data are needed. In the past these coefficients have been difficult to determine for lack of suitable experimental facilities. A new experimental approach involving simultaneous weight and strain measurement under a wide variety of environmental conditions is described. This approach is shown to elucidate questions on the effect of boundary conditions (critical for adequate determination of cross coupling coefficients).

THEORY

Dimensional changes or strains $\delta_{ij}$ of composite materials are typically calculated from the inverse Duhamel-Newman uncoupled constitutive relation:

$$\varepsilon_{ij} = \varepsilon_{ij}^o + S_{ij}^{kl} \sigma_{kl} + \alpha_{ij} \dddot{T} \delta_{ij} + \beta_{ij} \dddot{M} \delta_{ij}$$

(1)

$\alpha_{ij}$ = linear coefficients of thermal expansion (CTE or LCTE)

$\beta_{ij}$ = linear coefficients of moisture expansion (CME or LCME)

$\sigma_{kl}$ = applied stresses
\[ \delta_{ij} = \text{Kronecker delta (0 if } i \neq j, 1 \text{ if } i = j) \]

\[ S_{ij}^{ki} = \text{elastic compliance matrix} \]

The non-mechanical dimensional strains \( \hat{\varepsilon}_{ij} \) due to moisture absorption can be predicted (at a fixed temperature) for orthotropic composite laminates when we assume a valid Kirchoff hypothesis and a plane stress state: \( \hat{\varepsilon}_{zz} = \hat{\varepsilon}_{xz} = \hat{\varepsilon}_{yz} = 0 \). For simplicity we shall consider only midplane symmetric laminates extended in the \( 0^\circ \) or \( x \)-direction:

\[
\hat{\varepsilon}_x = a_{11} N_x + a_{12} N_y + a_{16} N_{xy} \tag{2}
\]

\[ a_{ij} = \text{compliance matrix} \]

and \( N_i \) are the hygric force resultants per unit \( \bar{\Delta}M \), summed over each kth ply;

\[
N_x = \hat{O} (Q_{11} \hat{\varepsilon}_x + Q_{12} \hat{\varepsilon}_y + Q_{16} \hat{\varepsilon}_{xy}) (z_k - z_{k-1}) \tag{3}
\]

The \( Q_{ij} \) are the reduced stiffnesses. We see that this prediction requires knowledge of the sample stiffnesses, dimensions, layup, and the ply values \( \hat{\varepsilon}_x, \hat{\varepsilon}_y, \) and \( \hat{\varepsilon}_{xy} \). This standard approach assumes that neither the stiffnesses nor the CME values change with time, moisture content or temperature. We have found, for example, that in cyanate esters the absorption continues for very long times, implying a relaxation process very likely to be accompanied by stiffness changes. In view of these uncertainties, it is often preferable to measure the CME of the laminate.

**CONVENTIONAL CME TESTING**

Since mass diffusivity is many orders of magnitude less than the thermal diffusivity, greater care is required to achieve equilibrium moisture (versus temperature) conditions. A convenient method for determining the CME (Norris [1]) is to dry the sample, and weigh it intermittently while it absorbs moisture under a prescribed humidity condition until it saturates. Figure 1 gives typical \( 0^\circ \) or \( x \)-direction absorption data (air at 24 deg C with 35% relative humidity) for two thicknesses of a pseudo-isotropic plate (M55J/954-03, with [0/-45/45/90], and [\}], layups.) The 954-3 is a toughened aromatic cyanate ester resin which absorbs 4-5 X less water than a typical epoxy system such as Fiberite’s 934 resin [2]. The strain change was measured during dryout (air at 24° C with 0% R.H.). The ratio of the equilibrium strain to the equilibrium moisture content is the CME. There are two problems here. First, this approach assumes that absorption and desorption are completely reversible, at least for one cycle. Second, depending on the specimen thickness and the need to stay below the \( T_g \) of the matrix, these measurements can be very time consuming - to periods of months. To save some time, the (incomplete) strain curve during desorption can be extrapolated to infinite time by assuming it will be proportional to the moisture content of the sample. This is done by plotting strain versus the fractional average moisture content change \( G \), (Shen and Springer [3]) where \( G \) is approximated by:

\[
G = \left( M - M_o \right) / \left( M_e - M_o \right) = 1 - \exp \left[ -7.3 \left( D t / s^2 \right)^{0.75} \right] \tag{4}
\]

"\( s \)" the sample total thickness when diffusion is from both sides.

A linear regression curve is extrapolated to \( G = 1 \), where \( t = \), equivalent to the equilibrium strain. Figure 2 shows a typical series of desorption and strain extrapolation curves. Equation 4 requires an accurate knowledge of the diffusivity \( D \). This can be calculated from the initial slope of the absorption curve and knowledge of the maximum or equilibrium moisture content [3]. The complete initial absorption curve (e.g., Figure 1) is therefore required for this approach.
Since we extrapolate by assuming moisture-strain proportionality in any case, we have considered whether strain-mass changes are proportional at short times and thus could yield the CME quickly. We have also noted that some materials such as many cyanate ester matrix composites continue to absorb for periods up to a year. This means that one can not correctly use the extrapolation referred to above as the wrong diffusivity will be calculated when the equilibrium moisture content is unknown. Use of short term data to obtain the CME is consequently desirable. Wolff [4] has shown that for a thin laminate with a low number of plies, and depending on the layup, the strain can not be proportional to the total moisture content during either ab- or desorption (before equilibrium has been achieved). However, for thicker samples and/or for more isotropic layups, the assumptions for equations 1-3 apply. We thus assume:

$$\hat{\alpha}(t) / M(t) = \hat{\alpha} / M = \hat{\alpha}$$

(5)

The data from Figures 1 and 2 were analyzed for short times \( t < 100 \text{ hrs} \). Figure 3 uses a linear regression fit to short term data. Table I summarizes short term versus long term data. These results appear promising as the CME can then be measured (at ambient temperature) in a period of less than 50 hours. Unlike the extrapolation for \( \hat{\alpha} \), it is not necessary to assume Fickian diffusion. Further implications of Eq.5 include that if one knows \( D(T) \), perhaps from another sample, and measures just \( \hat{\alpha}(t) \), one can calculate \( M(t)/M \) [5] and hence \( \hat{\alpha}_0 \) and then \( \hat{\alpha} \). It is noted that all the data above were obtained with samples starting with an equilibrium or uniform
moisture distribution. However, if the conditions above (plane stress state etc.) hold, the results should be equally obtainable with an arbitrary initial moisture distribution as long as the moisture content and strain change measurements cover the same average moisture content change. An initial survey of other test data suggest that the short term accelerated CME approach is valid for laminates with unidirectional plies and various layups from them, but that the use of hybrid composites and woven layers may complicate the situation. Further work is required here.

Further reduction in measurement time would be accomplished by measuring the strain and weight change simultaneously (on the same sample). This would also allow detection of possible changes in CME on moisture cycling or during the presence of a second plateau in an absorption curve. (Plateaus and continues absorption have been found for cyanate ester composites after several months at ambient temperatures). Development of such a technique would also facilitate the evaluation of boundary conditions (e.g., flowing dry air vs. vacuum), various geometries (e.g., fibers) and cross coupling coefficients in the general field of hygrothermoelasticity.

The objectives were as follows; strain, weight, temperature and humidity must be continuously measurable in a controllable environment which must include vacuum, still or flowing gases and controlled relative humidity. One must be able to change the humidity instantaneously while.

**SIMULTANEOUS STRAIN AND WEIGHT MEASUREMENT**

Fig.2  Desorption strain at 24°C and 0%RH of two laminates extrapolated to G = 1(t = )
Fig. 3 Desorption strain from Figure 2 analyzed for short times.

Table I Summary of accelerated vs. equilibrium CME for two laminates

<table>
<thead>
<tr>
<th></th>
<th>Sample I</th>
<th>Sample II</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusivity (mm$^2$/s)</td>
<td>3.08e-7</td>
<td>3.6e-7</td>
<td>1</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>1.106</td>
<td>2.032</td>
<td></td>
</tr>
<tr>
<td>Equilibrium M (%)</td>
<td>0.10</td>
<td>0.10</td>
<td>1</td>
</tr>
<tr>
<td>Equilibrium strain (µε)</td>
<td>3.0</td>
<td>2.8</td>
<td>2</td>
</tr>
<tr>
<td>Equilibrium CME (ppm/%M)</td>
<td>30</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Strain for t$^{1/2}$ = 600 s$^{1/2}$</td>
<td>2.1</td>
<td>0.78</td>
<td>3</td>
</tr>
<tr>
<td>M for t$^{1/2}$ = 600 s$^{1/2}$</td>
<td>0.072</td>
<td>0.037</td>
<td>1</td>
</tr>
<tr>
<td>CME at t$^{1/2}$ = 600 s$^{1/2}$</td>
<td>29.2</td>
<td>21.1</td>
<td></td>
</tr>
</tbody>
</table>
keeping the temperature constant and vice versa. These changes must be possible with simultaneous changes in the stress state. The standard CTE, CME data together with mass diffusivities must be obtainable on the same system. Temperature gradients must be sustainable. A means to apply stress to the sample is also desirable. Accuracy and resolution must be on the order of \(10^{-4}\) g and \(10^{-7}\) m.

**EXPERIMENTAL DEVELOPMENT**

The best candidates for detection of microgram weight changes are microbalances and quartz springs. While the former can operate well at constant pressure there are problems with a change, for example, from flowing dry air to vacuum in the same system. Consequently, spiral quartz springs were adopted.

Strain change techniques include mainly electrical transducers and optical techniques. We require a minimal contacting method which is also insensitive to a variable environment of temperature and pressure. Interferometry is limited by variations in indices of refraction. An optical intensity integrating reflective technique was found to be sensitive to IR emission changes of the system container. Piezoelectrics do not currently have the necessary range.

Stress application is difficult as it may interfere with continuous weighing. One approach was to use a wire to impart a flexural stress [6] and this wire becomes a small constant additional weight to the system. Tensile stresses to several GPa can be imparted to fibers, some of which were recently reported to exhibit substantial negative CME values [7].

Figure 4 shows the basic principles of an athermalized measurement system described in more detail elsewhere[8]. A precalibrated quartz spring (spring constant 280 l g/m with capacity of 30-50g) supports a plate sample above an LVDT core which in turn is raised/lowered by a motorized actuator. A small (0.07 mm or smaller) horizontal copper wire is attached via colloidal silver paint to each end of the sample for electrical contact. This could be part of a thermocouple to measure the temperature of the ends of the sample. As the LVDT core is raised, a reading is obtained at first contact equal to:

\[
\bar{a}_1 = -\bar{a} (\Delta L \text{due to CTE}) + \bar{a} (\Delta W) + \bar{a} (\Delta L \text{due to CME}) \tag{6}
\]

Further raising causes the top of the sample to make contact with the conducting stop. This reading represents:

\[
\bar{a}_2 = -\bar{a} (\Delta L \text{due to CTE}) + \bar{a} (\Delta L \text{due to CME}) \tag{7}
\]

The difference \(\bar{a}_1 - \bar{a}_2\) equals \(\Delta W\) via the spring constant and at constant temperature, \(\bar{a}_1\) represents the \(\Delta L\) or \(\bar{a}_1\) due to the CME. A special circuit accounts for spring oscillations and a thermoelectric cooler keeps the LVDT at a controlled temperature. The entire system is supported by a quartz tripod in an environmental chamber which can vary pressure, temperature, gas flow rate and humidity. A double heater allows imposition of temperature gradients for studies of their effects on mass flow.

**RESULTS WITH SIMULTANEOUS WEIGHT/STRAIN**

Initial measurements were made at 63°C on a graphite/epoxy plate 254 mm long by 50 mm wide and 0.75mm thick. It was an M55J/RS-3 unidirectional laminate measured in the 90° direction. After stabilization to the nearest 0.1 mg at 54%RH and 25°C, the sample was placed in the system of Fig. 4 at 63° +/- 1°C and held for about 4 days. Figures 5-7 indicate small initial scatter in the readings of \(\Delta L/Lo\) and \(\Delta M\). The ratio of the linear regression curves to these data
gives the CME or \( \hat{\alpha} \), shown in Fig. 7. The value of 3046 ppm/%M is slightly higher than the equilibrium value of 2560 ppm/%M obtained at 24°C on the same sample. Further work is needed to ascertain whether this is a function of temperature, aging or storage time (several years) or non-Fickian diffusion.

![Basic elements of a simultaneous weight-strain system](image)

**DISCUSSION**

A major direction for investigation is the question of strain-moisture content proportionality at longer times. The moisture absorption of some systems does not stabilize at longer times but may either steadily increase with time (at least for a year) or exhibit secondary plateaus. These effects are often attributed to relaxation processes in the polymer and hence one might detect changes in the CME. Additionally, thermal and/or moisture cycling may cause changes in sample porosity, microcracking and debonding at the fiber/matrix interface. These effects at first glance should exhibit increased moisture ab- or desorption with a lesser effect on dimensional changes; hence a lower CME. Sudden environmental changes may involve, for example, rapid drying of the surface causing surface layer shrinkage, or increased surface density and hence an effective surface barrier against further drying (diffusion). We have detected all of these changes in graphite/polymer matrix composites and with a means of simultaneous strain/weight change measurement hope to further elucidate their effects on CME.
There is a need to measure various cross coupling coefficients between mass and heat flow, $a$, $a$, stress, $T$, and their gradients and rates of change. For example, the Soret effect is a mass flux caused by a temperature gradient; the Dufour effect is heat flow caused by a concentration gradient. Sih [9] has measured these cross coupling coefficients for T300/5208. Szekeres et al [10] have also extended these considerations to mechanical effects. Toman [11] has suggested that cross coupling coefficients may be detectable by observing deviations from Equation 1. However, few cross coupling coefficients have been measured, mainly because of lack of suitable experimental facilities and a need to define the boundary conditions.

![Graph](image)

Fig. 5 Short-term strain at 63°C for a unidirectional laminate measured in 90° direction

**CONCLUSIONS**

Short term strain and moisture absorption data gives a good approximation of the (equilibrium) CME for many laminated fiber reinforced composites. If the diffusivity is known, then only the strain needs to be measured for relatively short times to give an equilibrium CME. These considerations assume that Fickian diffusion predominates. Further work is needed to clarify
longer term effects on CME such as polymer relaxation and microdamage. Simultaneous measurement of weight and strain changes will help to clarify the effects of moisture cycling, long term continued absorption and secondary absorption plateaus on the CME. They also provide a potential means to study cross coupling coefficients and boundary effects. A system for simultaneous measurement was developed and initial testing appears promising.

\[ y = -1.126 \times 10^{-3}x \]
\[ R^2 = 7.001 \times 10^{-1} \]

Fig. 6   Simultaneous weight change for sample of Fig. 5

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Fig. 7  CME from ratio of linear fits to data of Fig.5 and Fig.6

REFERENCES


